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Ozonation of a Municipal Surface Water Supply to Reduce Odor and Enhance Flocculation

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OZONATION OF A MUNICIPAL SURFACE WATER SUPPLY TO REDUCE ODOR AND ENHANCE FLOCCULATION

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TO REDUCE ODOR AND ENHANCE FLOCCULATION

This thesis is approved as a creditable and independent investigation by a candidate for the degree, Master of Science, and is acceptable for meeting the thesis requirements for this degree. Acceptance of this thesis does not imply that the conclusions reached by the candidate are necessarily the conclusions of the major department.

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OZONATION OF A MUNICIPAL SURFACE WATER SUPPLY

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Abstract

DAVID EDWARD NUSZ

The city of Huron, South Dakota, draws its drinking water supply primarily from the James River, a stream of extremely variable water quality which is difficult to treat. In this research, ozone was applied to the raw water through use of a pilot plant to determine what effects ozonation has on odor and flocculation.

Following a preliminary study based on trihalomethane reduction, ozone dosages of 0, 4, 8, 12, 16 and 24 mg/l were applied to the raw water at a 20-minute contact time. Threshold Odor Tests were performed by an odor panel to obtain qualitative descriptions and quantitative measurements of odor intensity of raw and ozonated water samples. Odor tests were also performed on settled jar-test samples. The flocculation study also utilized jar tests. Constant dosages of chemicals used at the Huron plant were added to both raw and ozonated water samples in the jar-test procedure. The settled samples were analyzed for turbidity which was assumed to be a direct function of flocculation efficiency. In addition to turbidity values, visual observations of flocculation were also noted.

Although aeration alone did not improve or reduce the odor, ozone consistently changed the odor of the raw water from one described as "fishy" to one described as "pleasant" or "sweet". Odor intensity was also substantially reduced in most cases. Because of the characteristic

odor change, ozone dosages of 4 or 8 mg/l are probably adequate for most odor applications at Huron. Due to variability and inconsistency encountered in the flocculation study, a valid conclusion regarding the effectiveness of ozone in reducing turbidity could not be made. However, ozonated raw water, at the higher dosages, produced larger floc particles that formed more quickly and settled more readily than in corresponding samples of untreated water.

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INTRODUCTION

The purpose in applying ozone to the raw water supply at Huron, South Dakota, was to determine specific effects ozonation has on the water quality. A pilot plant was used to investigate trihalomethane formation, chlorine demand, total organic carbon, odor, and flocculation. Odor control and flocculation enhancement via ozonation are discussed and analyzed in the forthcoming pages. The remaining objectives will be described by Bedessem.

Nature of the Problem

Odor

Sources of odors in drinking water supplies are of natural and/or industrial origins. The natural causes of odors in water supplies include vegetation, decomposed organic matter, mineral substances, and hydrogen sulfide, but the most frequent offenders are algae (44)(51).

Algae are simple forms of plant, or plant-like, organisms found mostly in lakes, ponds, and reservoirs. At times, the odor caused by the oils liberated by such microscopic plant growths is extremely intense and disagreeable. The taste and odor are variable according to the particular algae involved, the most common being grassy, moldy, earthy, fishy, and aromatic odors (48).

Continued biological activity upon dissolved organic materials will produce low-molecular-weight volatile compounds which can possess an odor (31). Only rarely does a water source contain a single, isolated odorant (24).

Odors from industrial sources typically have their origin with synthetic organic compounds, although some inorganic chemicals can contribute to odor problems (47). Odors may arise in several ways. First, the waste may contain some odorous substances like phenols or pyridine. This is true of all organic-product processors. Second, the waste may contain substances which, under anaerobic conditions, decompose and produce odors. This applies particularly to all of the wastes of food and beverage processing. Third, the waste may contain substances which react with constituents in the water to produce odors. Examples are the phenolic substances which react with chlorine to form chlorophenols, and the reduction of sulfates to form hydrogen sulfide and mercaptans (51).

Odor is recognized as a quality factor affecting water in several ways: acceptability of drinking water (and foods prepared therefrom), tainting of fish and other aquatic organisms, and aesthetics of recreational waters (47). With such a wide variety of chemicals causing taste and odor problems, it is impossible to effectively name one economic, efficient treatment method. Although chlorine and activated carbon have been widely accepted treatment methods, potassium permanganate, chlorine dioxide, and ozone have recently become popular for specific applications (44).

A standard method for measuring odor intensity is the Threshold Odor Test (47). Odor tests are useful as a check on the quality of raw and finished water for various uses such as the determination of treatment dosages, testing treatment effectiveness, and tracing contamination sources (51).

Flocculation

Because a large portion of the suspended particles in water are too small to allow removal by simple sedimentation, the treatment of water, especially surface water, usually includes flocculation (46)(48). Flocculation is the process by which the negatively charged colloidal particles in the water (on the order of one micron in diameter) are agglomerated.

To produce aggregates large enough to be removed by conventional treatment, colloidal particles may be brought into contact by Brownian diffusion of the individual colloidal particles and by fluid motion. The total number of contact opportunities are a function of the flocculation rate, detention time, floc volume fraction, and collision efficiency (44). Successful flocculation requires consideration of all these parameters.

Chemicals initially used to destabilize colloidal particles include aluminum sulfate (alum), ferric chloride, ferric sulfate, sodium aluminate, ferrous sulfate and lime, and chlorinated copperas. However, alum is the most commonly used chemical. Polymeric coagulants, or polyelectrolytes, are long-chain high-molecular-weight molecules bearing a large number of charged groups which are also used in the coagulation process (37)(44).

Several agents are used to enhance the flocculation process. The agents include oxidizing agents, weighting agents, activated silica, and polyelectrolytes (48).

Oxidizing agents are thought to enhance flocculation by the oxidation of organic compounds which would normally interfere in the process.

Weighting agents such as clay increase the particle density and average weight. Activated silica acts as a bridging agent and may produce very large agglomerated particles. Polyelectrolytes, as well as being used as coagulants, have applications as flocculant aids because they also act as bridging agents.

The selection of the type and dosage of coagulant and flocculant aids is usually made on the basis of a series of batch tests, commonly referred to as standard jar tests. Besides the jar tests, two other relatively new methods are used to monitor coagulation and flocculation, the zeta potential and the pilot filter (33)(37).

Scope of the Investigation

Huron draws its drinking water supply primarily from the James River, a tributary of the Missouri River. Minimal flows of the James often reduce the source to a stagnant pool of water. A 27-year history of the river revealed no flow approximately 40 per cent of the time; a flow of less than 30 cfs (0.8 m^3/s) 75 per cent of the time; and annual average flows of 259 cfs (7.3 m^3/s) (35).

The flow variations result in water of extremely variable quality which is difficult to treat. As a result of a no-flow situation, plant personnel stated that the water encountered during the odor research period (June 29 to July 16, 1981) was as bad as any during the year.

Odor tests were performed to obtain qualitative descriptions and quantitative measurements of odor intensity relative to various ozone dosages. In the odor research, odors of raw- and ozonated-water samples were compared. Jar tests were also utilized. Typically, various

chemical dosages were added to a series of water samples during a short period of rapid agitation. Following slow stirring and settling periods, odor was measured.

Jar tests were also used in the flocculation research. Following chemical additions, stirring, and settling, the water samples were each measured for residual turbidity. These turbidity values were then used to determine flocculation characteristics of the ozonated and unozonated samples.

LITERATURE REVIEW

Background

History of Ozonation in Water Treatment

Various authors have summarized the history of ozone use in water treatment (12)(13)(26)(29)(36).

Ozone was first reported by Van Marum in 1785 when he noticed a peculiar odor in the vicinity of electrical machines. In 1801, Cruickshank observed the same odor in the gas formed at the anode during the electrolysis of water. Schonbein named ozone in 1840, claimed its presence in the earth's normal atmosphere, and experimented with ozone for water treatment at Metz, Germany. Werner von Siemens originally designed an electric-discharge ozone generator in 1857. Brodie, in 1872, definitively showed ozone to be a triatomic molecule of oxygen.

DeMeritens investigated ozone as a germicide for the sterilization of water. A few years later, Foolich reinvestigated the subject and erected a plant at Martinikenfeld, Germany. In 1892, the first drinking water treatment plant to employ ozone was erected at Oudshoorn, Holland. Studies by Ohmuller and Prall at the request of the German government led to full scale municipal plants at Wiesbaden and Paderborn in 1896.

A group of French doctors studied the Oudshoorn plant and its ozonated water and, after pilot testing at the St. Maur plant in Paris, a plant was constructed at Nice, France, in 1906. Because ozone has been used continuously at Nice since the Bon Voyage plant began operating in 1906, Nice is referred to as "the birthplace of ozonation for drinking water treatment".

Full-scale water treatment plants were then constructed in several European countries. As of 1916, there were 49 treatment plants in operation. By 1940, 119 water treatment plants utilized ozonation. As of 1980, the total number of water treatment plants employing ozone exceeded 1,100.

The first plant in the United States to use ozone was constructed in 1927 at Delhi, New York. Initially, plants were also constructed at Long Beach, Indiana; Hobart, Indiana; Denver, Pennsylvania; and Whiting, Indiana (13). The Whiting plant has used ozone continuously since 1940 for taste and odor control. Although interest in ozonation for drinking water treatment is on the increase, the United States had eight plants utilizing ozone as of January, 1981, with three more under construction (42).

The extensive use of ozone in Europe is related to the poor quality of their potable water resources and to their desire for a high quality of drinking water. The use of ozone in the United States during the last decade has increased because of similar reasons and also because of more stringent water quality standards (31).

Water treatment philosophies in Europe differ significantly from those in the United States (29). In addition to being chemically and biologically safe, Europeans expect their drinking water to be free of foreign taste, odor, and color. In the United States, treatment philosophy is based on the production of water that is bacteriologically safe, but little emphasis has formerly been placed on the removal of adverse tastes, odors, and potentially harmful chemicals.

Ozone Characteristics

If oxygen or air is passed through an electric discharge or exposed to certain wavelengths of radiation in the ultraviolet range, some of the oxygen is polymerized and ozone is produced following the reaction (20):

$$3\ O_2 \rightarrow 2\ O_3 \qquad (1)$$

Ozone is an unstable allotrope of oxygen that will quickly react with many oxidizable substances. The ozone molecule is made up of one central oxygen atom attached to two equidistant oxygen atoms. The included angle is 116^{o} 49' and the bond length is 1.278 Å (1). Ozone is a powerful oxidant second only to fluorine among readily available water treatment chemicals and has an oxidation potential of 2.07 volts. Ozone has a characteristic penetrating odor which is readily detectable at concentrations as low as 0.01 parts per million (ppm) by volume (20) (29)(43). The suggested limit in air for safety purposes is 0.1 ppm.

Ozone boils at -170^{o}F (-112^{o}C) and is 1.5 times as dense as oxygen but thirteen times more soluble in water (8)(42). However, because of a much lower available partial pressure, it is difficult to obtain an ozone concentration of more than a few milligrams per liter (mg/l) under normal conditions of temperature and pressure (20).

Ozone should be considered a dangerous gas because of its capability of oxidizing organic materials. At the relatively low concentration of ozone produced by commercial equipment (1 to 3 per cent in air; 2 to 6 per cent in oxygen), no explosive hazard exists (29). However, mixtures of ozone in air can be explosive if concentrated to 15 to 20 per cent.

In aqueous solutions, ozone is relatively unstable, having a half-life of 20 to 30 minutes in distilled water at 68°F (20°C) (29). As a result, it must be produced and used at water treatment plants. On the other hand, ozone in air is much more stable than in water. Normally, the half-life of ozone in ambient atmosphere has been determined to be approximately 12 hours. However, the more dilute the ozone, the slower the dissociation. Axeworthy and Benson (39) found that a sample containing 5 per cent ozone in an atmosphere of oxygen could be stored at room temperature for nearly two months before the ozone concentration would fall below 4 per cent.

According to Mignot (28), the action of ozone on the dissolved or suspended matter contained in water is based on oxidation, ozonolysis, and catalysis. The oxidizing power of ozone is characterized by the addition of one atom of oxygen. By ozonolysing, ozone can react upon double bonds by fixing its complete molecule to the atoms connected together by a double bond; consequently, the initial molecule is broken down into two simpler molecules. Finally, by its catalytic action, ozone accelerates oxidation rates.

In air, ozone decomposition is greatly accelerated by heat. However, both the mechanism and kinetics of the dissociation of ozone in water are uncertain, although Weiss observed that decomposition increases rapidly with increasing alkalinity (39).

Ozone is unstable and has a tendency to divest itself of its third oxygen atom through:

$$O_3 \rightarrow O_2 + O \text{ and } O + O \rightarrow O_2 \qquad (2)$$

Based on an extensive review of the literature, Peleg (39) suggested the following stages for ozone decomposition in aqueous solutions:

$$O_3 + H_2O \rightarrow O_2 + 2\ OH \quad (3)$$

$$O_3 + OH \rightarrow O_2 + HO_2 \quad (4)$$

$$O_3 + HO_2 \rightarrow 2\ O_2 + OH \quad (5)$$

$$OH + OH \rightarrow H_2O_2 \quad (6)$$

$$OH + HO_2 \rightarrow H_2O + O_2 \quad (7)$$

$$OH + OH^- \rightarrow O^- + H_2O \quad (8)$$

$$O^- + O_2 \rightarrow O_3^- \quad (9)$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \quad (10)$$

All of the intermediate species formed in the above equations (O_3, OH, O^-, O_3^-, HO_2, and H_2O_2) are very reactive and possess very short half-lives (39).

As can be observed, the decomposition behavior of ozone in water is complicated depending on the alkalinity of the solution and also on other parameters such as oxygen content.

Some fear highly toxic epoxides may form when chemicals such as DDT breakdowns react with ozone in water. However, Maggiolo recently told an ozone workshop that he simulated plant conditions with respect to the reaction problem. Finding it "impossible to get epoxy compounds in water", he looks more for ozone reaction products such as carbonyls, glycols, acids, and peracids, along with aromatic ring breakdown (38).

Nebel (32) also reported on ozone oxidation products. He said that intermediate oxidation materials containing organic functional groups such as aldehydes, ketones, alcohols, and organic acids can be formed.

Ozone oxidizes many of these materials which chlorine also attacks. This leads to a reduced chlorine demand and a reduction in the formation of chlorinated hydrocarbons such as trihalomethanes when chlorination is the terminal treatment process.

In addition, Hortemann, a noted French toxicologist specializing in water treatment processes, has shown that the oxidation products of ozone are less toxic and more biodegradable than the materials from which they were made (32). In short, suspected toxic products which could be produced by an ozone oxidation have not been found in ozonated surface water.

Ozonation Advantages and Disadvantages

Major advantages and disadvantages of ozone are listed in Table 1. Ozone is considered a viable alternative to chlorine for many European water supplies. On the other hand, chlorine is used almost exclusively in the United States. One reason for ozone's lack of popularity in the United States is that as a result of World War I research, chlorine was manufactured cheaply and in large quantities (26). Unfortunately, this is no longer the case. It should also be noted that until recently, ozonators have been expensive and problem-plagued. With technological developments, ozonator costs and maintenance requirements have steadily declined (26). In addition, ozonation systems are easily automated.

Ozone Applications

The use of ozone for drinking water treatment is largely related to its power as an oxidant. Because many raw water contaminants are oxidizable, ozone can be used for many specific applications. The major

Table 1. Ozone Advantages and Disadvantages in Water Treatment (9)(17)(25)(29)(34)(42)

Advantages	Disadvantages
Powerful oxidant	Nonselective oxidant
Action not appreciably altered by pH variations between 5.0 and 8.0 units	Temperature is important factor in rate of reaction and decomposition
Turbidity up to 5 mg/l does not affect disinfection characteristics	Ozone demand of water must be met before efficient disinfection occurs
Residual in water is easily measured	Leaves no residual in distribution system
Does not produce halogenated organic compounds	Must be produced and used at the treatment site
Easily detected by human nose before reaching toxic levels	Higher capital costs than simple chlorination

applications are listed in Table 2. It is important to realize that even though ozonation might be installed for a single purpose, many other side benefits can be derived from its use. For example, at three water treatment plants in West Germany, ozone's primary function is iron and manganese oxidation. At the same time, organics are oxidized, microflocculation is effected, and considerable predisinfection is obtained (42).

Similar benefits were reported by LePage (22) at the Monroe, Michigan, ozonation installation for taste and odor control. Subsequent studies have shown that various supplementary benefits of ozonation occurred simultaneously with the destruction of taste and odor. These included partial or complete disinfection, destabilization of certain colloids, enhanced flocculation with alum, better settling, cyanide destruction, and reductions in chlorine demand.

Because ozonation is a multi-purpose chemical process, ozone may be applied at various points in the water treatment scheme. To induce flocculation, it is usually introduced at a point early in treatment; to eliminate tastes and odors, at an intermediate point (43). If ozone is applied near the end of the treatment process, a significant amount of disinfection and color removal will be obtained. The conjunctive use of contactor off-gases from the primary ozone contacting chambers can be effective in such multiple ozonation treatment processes. These off-gases, which can contain as much as 5 to 10 per cent of the original dosage, can sometimes be recycled economically to an early-stage treatment step. Many plants employ this method (42).

Table 2. Applications of Ozone in Drinking Water Treatment (22)(29)(31)(42)

Bacterial disinfection	Viral inactivation
Taste and odor control	Color removal
Suspended solids removal	Algae destruction
Microflocculation of dissolved organic compounds	Improvement of settleability characteristics
Oxidation of trihalomethane precursors	Oxidation of iron, manganese, and heavy metals
Oxidation of cyanides, sulfides, and nitrites	Oxidation of phenols, detergents, and pesticides
Conversion of large molecular weight and less biodegradable organics into smaller and more easily biodegraded compounds	Preparation of granular activated carbon for biological removal of ammonia and dissolved organics

Table 2 indicates that two possible uses of ozone are for taste and odor control and flocculation enhancement. These two applications were reviewed in greater detail.

Taste and Odor Control

Most tastes and odors in water supplies have their origin with either naturally occurring organic materials or synthetic organic compounds. Ozone oxidizes such compounds in the aqueous phase. Although the terms "taste" and "odor" are often used jointly, taste and odor problems in water supplies are concerned almost entirely with just odors (24). The manner in which ozone attacks the molecules of malodorous substances involves a very fundamental principle.

The molecules of odoriferous compounds are all electron-rich, while the ozone molecule reacts chemically as if it is electron-deficient (30). When the two types of molecules are brought into contact, an oxidation-reduction reaction takes place. Oxygen from the ozone saturates the excess electron sites of the molecules of the malodorous substances. In this reaction, ozone is reduced to oxygen and the third oxygen atom is attached to the odor-forming molecule, lowering its threshold odor.

Generally, low concentrations of ozone will produce large reductions of taste and odor, although higher optimum concentrations are sometimes required. The degree of oxidation attained depends on the amount of ozone employed and the contact time (22). It should be noted that the destruction of taste- and odor-causing compounds by ozonation does not imply their total oxidation to carbon dioxide and water (42).

Ozone dosage levels used for potable water treatment are not sufficient to accomplish such treatment (32).

It is important to recognize that ozone is not effective in all odor control applications. Nebel and Forde (30) reported that acetic acid, ammonia, sulfur dioxide, and saturated hydrocarbons are four compounds which ozone will not "deodorize". It is also important to consider the effect of the mixture of odorants present in a water supply. Two or more chemical odorants in an aqueous solution may induce one of three types of phenomena (24):

Additivity:	the resulting odor may be the sum of the individual contributions
Synergism:	the resulting odor may be greater than expected by direct addition
Antagonism:	the resulting odor may be less than expected by direct addition.

Ozone effectiveness must be evaluated for all three possibilities.

There are many examples of ozone effectiveness in the treatment of tastes and odors in drinking water. A brief review is presented here.

The extensive use of ozone originated in France, where ozonation has been used for about 75 years. Gomella's (9) report, "Ozone Practices in France", presented optimum ozone treatment techniques. He pointed out that ozone completely destroyed or markedly reduced many organic pollutants. Ozonation combined with post-chlorination eliminated any organoleptic taste and odor problems. At the Choisy-Le-Roi plant in Paris, an ozone concentration of up to 22 mg/l is used to treat polluted raw surface water. Taste and odor treatment was reported excellent.

Ozonation has also been successfully used in the removal of tastes and odors from Irish waters (36). Whitson, an experienced water plant operator, reported, "Over a 12-year working period, with the algal content of the water varying in variety and intensity, ozone has removed or reduced tastes and odors and sweetened others. There have been no complaints from consumers on this score and that is the best measure of success."

In 1972, Sommerville and Rempel (45) published the results of their pilot plant study on Shoal Lake water, a potable supply for Winnipeg, Canada. They determined that a Threshold Odor Number (TON) reduction of 50 per cent was directly attributable to ozonation. Ozone dosages up to 10 mg/l were used. Also in Canada, Montreal's new $300 million water treatment plant, the largest in the world to employ ozone (250 MGD), uses ozonation to improve taste and odor (21).

Ozone treatment for taste and odor control is not foreign to the United States. According to Powell et al. (40), the waters of the Iowa River have objectionable tastes and odors that are difficult to treat. Conventional treatment removes practically all of the original taste and odor, but replaces them with medicinal or chlorinous types. Powell and his co-workers concluded that ozonation satisfactorily removed tastes and odors in Iowa River water when the raw water threshold odor values were high but was of little use when they were moderate to low.

In 1935, Ferkinhoff (7) published a report describing ozonation at Hobart, Indiana. Before installation of the ozone system, finished water had taste and odor problems. After ozone system installation, the problems were virtually nonexistant.

Philadelphia's Belmont Plant applied ozone to raw water for taste and odor control from the early 1940's until 1959. McLaughlin (27) stated, "Ozonation not only reduced the odor quantitatively, but effected a change in the characteristic of the residual odor." The finished odor was nearly always described as "sweet", "flowery", or "balsamic". Bean indicated that the ozone treatment was discontinued when the plant capacity was increased and the use of free residual chlorination became more economical (24).

Of the eight water treatment plants in the United States presently employing ozone treatment, at least five enlist ozone primarily for taste and odor control (42). Of these, the city of Whiting, Indiana, has been using ozone the longest. Bartuska (2)(3) reported an average of 83 per cent TON reduction from the raw water (TON = 66) by ozonation alone during the 1940-41 operation. The dosage was not considered critical as long as a 0.1 mg/l ozone residual was maintained.

Besozzi and Vaughn also evaluated the effect of the ozone treatment as a taste and odor control at Whiting (24). Their results showed that during 21 days in March, 1947, ozone reduced the average TON of the raw water from 36 to 23, thereby removing 36 per cent of the odor. They concluded that ozone proved incapable of combating the taste and odor problem at Whiting because of its limited effectiveness.

The city of Monroe, Michigan, obtains its water from the shallow extremities of Lake Erie. In 1975, LePage (23) initially reported the results of an ozone pilot plant study aimed at solving the persistent odor problem. The most severe odors recorded at Monroe since 1972 had had threshold values of only 8 and were usually described as those

resembling oil refinery waste. Occasionally, musty odors would also reach that intensity. These odors were eliminated in the pilot plant study by application of 1.0 to 1.5 mg/l of ozone to the raw water. If first subjected to chlorination, however, they became more difficult to remove even under improved conditions following pretreatment.

As a result of the predesign investigations, the city of Monroe built an 18 MGD plant that employs ozone for taste and odor treatment. In February of 1981, LePage (22) reported that "taste and odor problems are now past history". After continuous operation had started, taste and odor complaints dropped from a high of 100 on a single day to none.

In summary, application of a suitable oxidizing agent destroys oxidizable compounds thereby eliminating tastes and odors. Ozone can be particularly effective because (5)(14):

a) Ozone is the most powerful oxidant used in water treatment; it oxidizes organic compounds not affected by other oxidizing agents. Ozone reacts very rapidly, requiring no long period of detention before oxidation takes place.

b) Ozone does not form additional compounds. Thus, intensification of odors, such as often occurs when chlorine is added to water containing complex organic matter, is not caused.

c) An excess of ozone reverts in a few minutes to ordinary oxygen.

d) The fact that ozone is carried in a large body of air means that aeration takes place simultaneously with oxidation. Volatile compounds in the water contributing to taste and odor are removed.

It should be remembered that ozone use is site specific. Before considering ozone use in water treatment, a preliminary study should be

conducted to determine if ozonation is actually advantageous.

Flocculation Enhancement

In many waters, colloidal organic matter tends to hamper floc formation. Oxidation of the organic matter will upset colloidal equilibrium and increase flocculation efficiency (13)(48). Ozone, by virtue of its oxidizing power, converts organic colloids to simpler forms which reunite to form polymolecular aggregates that are essentially inorganic and negatively charged (45). This stage may produce colloidal turbidity. A small dose of electrolyte, usually 15 mg/l of alum or less, will react with the aggregates and permit the formation of microflocs with positive charges. Some coagulating properties of alum are attributed to its polar interactions with other polar or charged molecules. Therefore, the efficiency of organics removal by alum increases when the organics are oxidized by ozone to polar or charged species (14)(32)(45). Ozone dosages for this type of treatment are usually in the range of 0.2 to 1.0 mg/l (32)(46).

Floc particles formed as a result of such treatment may be removed by either filtration or sedimentation, depending on initial raw water quality (5). In general, filtration alone can only be used for raw water having low turbidity while sedimentation is required for water of poorer quality (8)(28).

In the sedimentation process, improved settleability can be attributed in part to the ability of ozone to destabilize colloids and make them more amenable to alum treatment. In addition to improved settleability, ozonation has been observed to increase the size of floc particles as well as decrease the number of them (32).

Although ozonation has not been installed for the primary purpose of aiding flocculation, ozone has been noted to aid in the process. Rice and his associates (42) reported that preozonation at the Rouen, France, water treatment facilities results in improved flocculation. Other examples are the three Dusselforf plants and the Duisburg and Wuppertal plants, all in West Germany, where ozone's primary function is iron and manganese oxidation. However, an additional benefit is that flocculation is positively affected.

Studies by the Los Angeles Department of Water and Power on the Owens River supply determined that preozonation enhances flocculation and the resulting removal of turbidity in their direct filtration process. Other benefits reported by Tate and Trussell (52) were water quality improvement, additional solids retention in the filter, and prevention of turbidity breakthrough under certain conditions.

In 1941, Bartuska (2) reported that alum usage at the new Whiting, Indiana, plant was reduced by approximately 20 to 30 per cent due to a 1.4 mg/l ozone dosage. Conventional sedimentation was used to remove the floc particles.

McLaughlin (27) reported the results of an ozonation pilot plant installed at Philadelphia's Belmont Plant. He stated, "A totally unanticipated effect was the improved coagulation observed during the Belmont tests. Effective coagulation was obtained, in the ozone pilot plant, with one-third to one-half less alum then needed at the (conventional) city plant." The improved flocculation-sedimentation was determined to be due strictly to the ozone addition and not to other parameters such as mixing differences.

LePage (23) reported on ozone pilot plant results at Monroe, Michigan, in 1975. Among other findings, he determined that jar tests indicated overall improvements in the coagulation, flocculation, and settling processes following the application of ozone prior to coagulation with alum. In experiments comparing straight alum coagulation to coagulation with alum following ozonation, it was found that the pre-ozonated water exhibited superior floc-forming characteristics with regard to time and floc size.

According to LePage, use of 2.0 mg/l of ozone cut the floc formation reaction time in half and it was shortened even more by a 3.0 mg/l dosage. The ozonated samples also developed a larger floc that settled more readily than the floc obtained in the nonozonated samples. Similar results were obtained at the unfavorable temperatures at or near $39^{o}F$ ($4^{o}C$). LePage also pre-adjusted the pH with sulfuric acid to a pre-established optimum (6.82 units) and found that the alum reaction was enhanced while the ozone effectiveness remained unaltered.

However, LePage's end results, measured in turbidity removal, were not significantly better for the ozonated samples and could not justify ozonation as a flocculant aid specifically for that purpose. LePage summarized that ozone's apparent ability to destabilize colloids, accelerate coagulation, and improve flocculation and settling make it a valuable tool for the treatment of colloidal waters, especially if it is already being applied for other purposes.

Costs of Ozonation

For many years, ozone has had a bad image based on an impression that it was dangerous to use, equipment occupied considerable space, and the process was not economical under any circumstances. However, if used in a multi-purpose role, ozonation may provide more effective and economical treatment than respective conventional processes (16).

The capital costs of ozonation systems can vary depending on the size of the system. Rice and his associates (42) reported comparative costs to be $500/lb ($1,100/kg) of ozone generation capacity per day for large installations while smaller installations were rated at $4,000/lb ($8,800/kg) capacity per day. An added cost is housing for the system, which can range from approximately 20 to 33 per cent of equipment costs.

Total capital and operating costs depend on energy demand, amount of maintenance, required amortization period, interest rates, and cost of energy (29). Of these parameters, the major cost of operating an ozone plant is usually for purchased electrical energy (22).

For ozone generation systems, electrical energy is generally required for the ozone generator and building heating, cooling, and lighting requirements. According to Gumerman, Culp, and Hansen (11), ozone generation using air feed requires 11 kW-hr/lb (24 kW-hr/kg) of ozone generated. For larger, oxygen-fed systems, the requirement is 7.5 kW-hr/lb (16.5 kW-hr/kg) of ozone generated. Other sources report approximately the same results (22)(42). These figures include oxygen generation, ozone generation, and ozone dissolution.

When dealing strictly with ozone production, a general observation is that about twice the power is needed to produce a given ozone concentration from air as compared to oxygen (26)(42). Up to 100 lb/day (45 kg/day) of ozone production is usually cost effective for air feed. However, a higher production rate yields to oxygen feed (11).

The low level of energy currently required to generate ozone marks an improvement in production costs. In 1906, the ozonation system at Nice, France, required 33 kW to generate 1 pound of ozone (42). In 1967, Bartuska (3) reported that almost 40 per cent of the additional cost of operating with ozone was saved by resultant economies in the use of other chemicals at Whiting, Indiana. He noted that this fact along with the water quality improvement led to real savings and benefit.

LePage (22) also noted that such secondary benefits emerge as economically important at the Monroe, Michigan, plant. The Monroe plant utilizes an air feed system. Total power requirements, including that used in an off-gas reinjection system, are 10.3 kW-hr/lb (22.7 kW-hr/kg) at 100 per cent of the total output capacity. The most time-demanding maintenance is keeping the building and equipment clean, a task which requires about four hours weekly for the 18 MGD ozonation installation.

When the versatility of ozone, its many applications, and its effectiveness in breaking down potentially harmful synthetic organics are considered, these operating costs can be justified. Also, Keller and Schaffernoth (19) reported that ozonation followed by activated carbon adsorption has been demonstrated in Europe to be one of the most cost-effective combinations for the simultaneous removal of ammonia and dissolved organic compounds from raw drinking water supplies.

Although the use of ozone is site specific with regard not only to application but also to economics, the single unit process of ozonation offers many of the treatment benefits frequently requiring a number of conventional unit processes. It is this fact that makes ozone a treatment alternative to be investigated solely on its merit and irregardless of intangibles such as better water quality.

METHODS AND MATERIALS

Preliminary Study

The main emphasis of this research was placed on evaluating the effect of ozone on odor control and flocculation enhancement. Concurrent research conducted by Bedessem emphasized, among other things, trihalomethane reduction via ozonation.

Because trihalomethane formation is related to the type and amount of organic material present in a given water supply, as is odor production, a decision was made to use those ozone dosages and contact times that showed a promising decrease in instantaneous trihalomethane formation. As a result of the preliminary study, applied ozone dosages of 0, 4, 8, 12, 16, and 24 mg/l at a 20-minute contact time were arbitrarily chosen for further study. The trihalomethane data are presented in Appendix C, Table C1.

Flocculation studies utilizing settled water turbidity values from the jar-test procedure were carried out at the above dosages and contact time. Then, odor control was analyzed during a second set of runs at these dosages and contact time. After these results were analyzed, an optimum ozone dosage of 24 mg/l was chosen for the final odor control and flocculation enhancement research.

Because of the highly variable water flows and quality of the James River, replicate investigations were not deemed necessary nor required from a statistical point of view.

Pilot Plant Description

The ozone pilot plant consisted of an air preparation system, an ozone generator, and two contact columns. Pictured in Figure 1 is the air preparation system and ozone generator. Figure 2 is a photograph of the contact columns. The system was supplied by Emery Industries, Inc., Cincinnati, Ohio.

Specific unit processes have been described in great detail by DeBoer (4) and Stoebner (50). A general overview is given here.

In preparation of the air for ozone generation, atmospheric air was initially filtered and compressed to a pressure of 100 psig (690 kPa gage) by the unit shown in Figure 3. After being cooled and stored in a pressure tank, oil, moisture, and dirt were removed from the compressed air by passage through a coalescer, desiccator, and prefilter. A pressure regulator, the final air preparation step, reduced the pressure to 15 psig (103 kPa gage).

The next process unit was the ozone generator. The generator was a tube-type, air-fed, water-cooled unit operating on a 60 Hz, variable-voltage power supply. The main components of the ozone generator were three stainless steel tubes enclosed in a single compressed-air module, which is shown in the foreground of the photograph illustrated as Figure 4. Centered inside each of the stainless steel tubes was a tubular glass dielectric into which was inserted a tubular stainless steel screen that served as a high-voltage electrode. Ozone was produced when clean, dry air from the air preparation system entered the module at one end and passed through the small annular opening between the glass

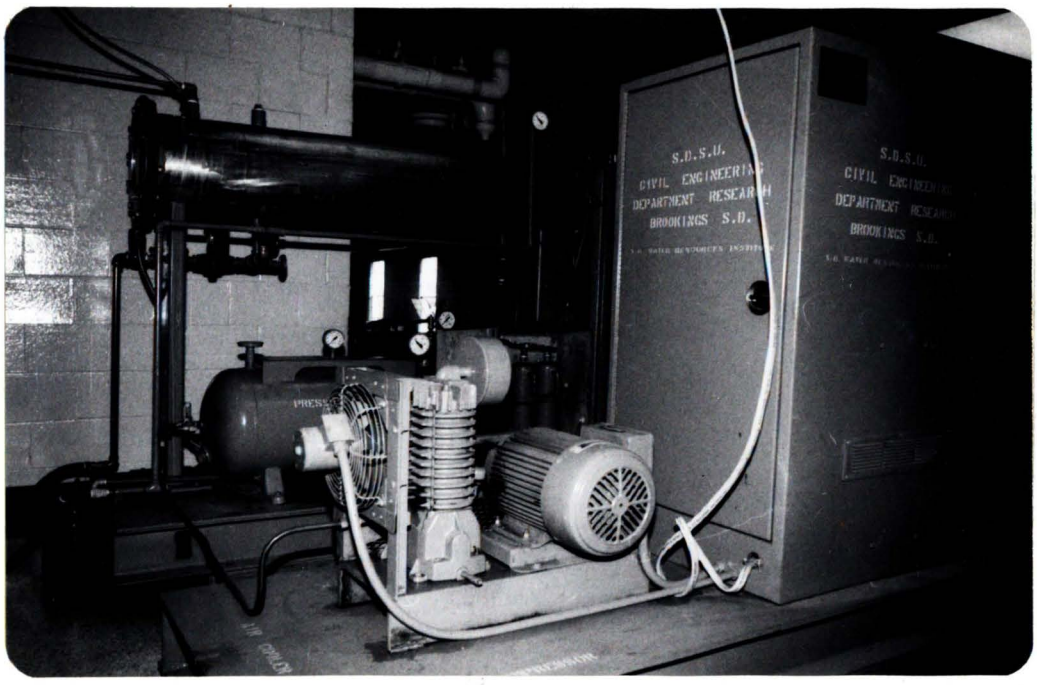


Figure 1. Air Preparation System and Ozone Generator

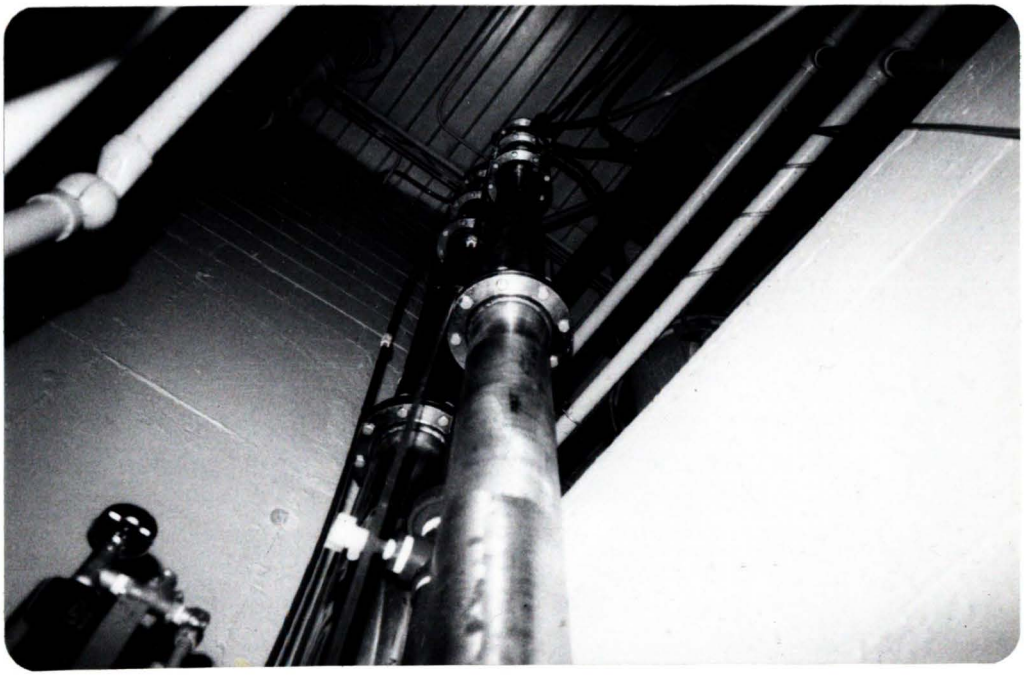


Figure 2. Ozone Contact Columns

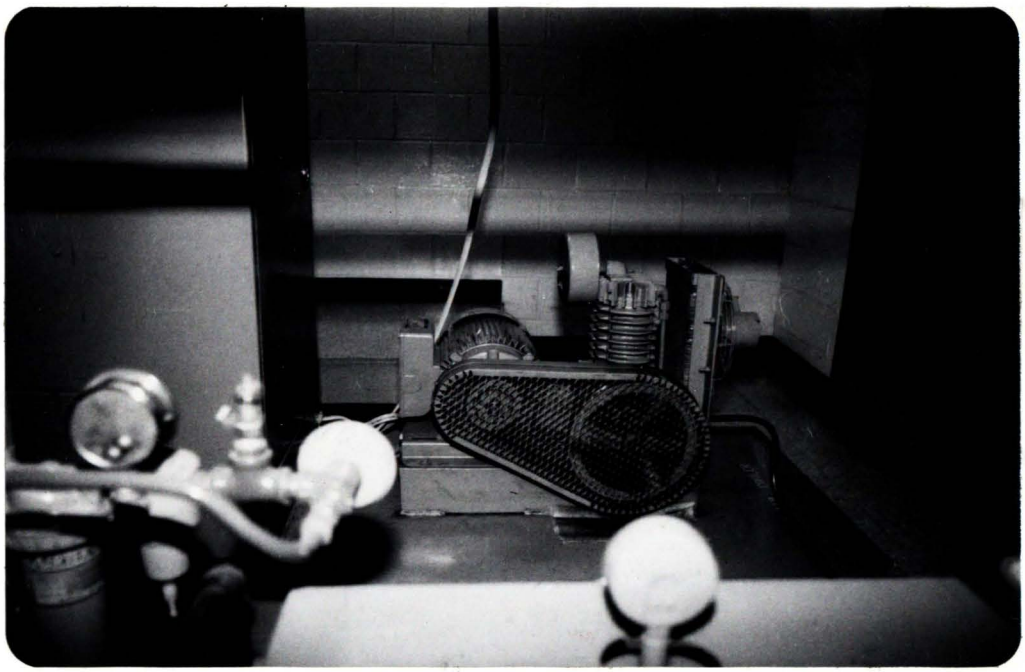


Figure 3. Preparation System Air Compressor

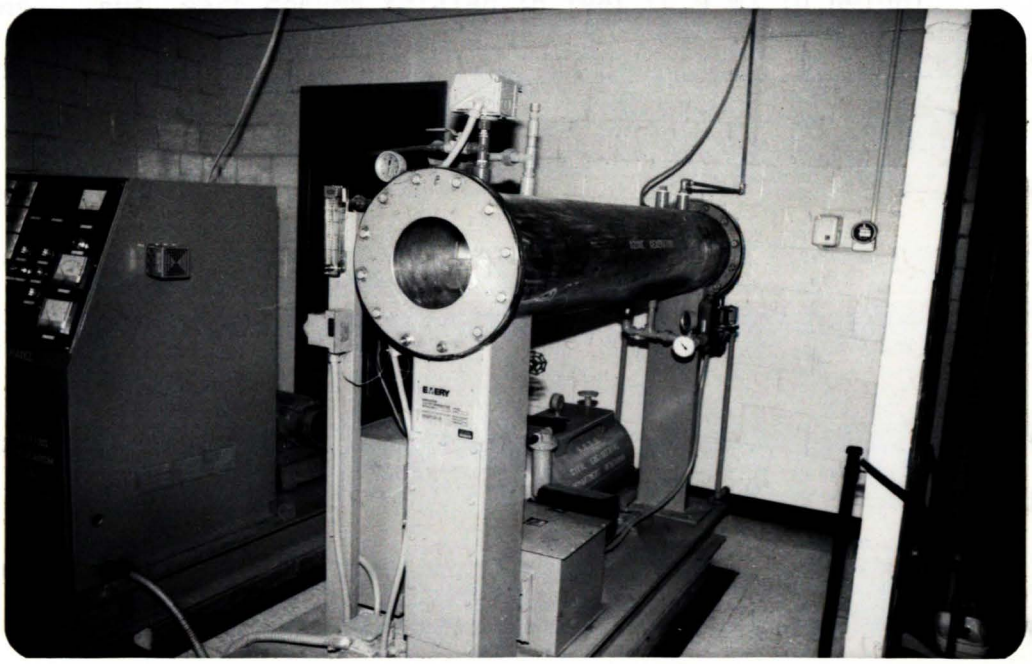


Figure 4. Ozone Generator Module

dielectric and the stainless steel tube. The corona discharge across this annular opening caused a small percentage of the oxygen in the air-feed gas passing through it to be converted to ozone. Heat generated by the corona discharge was removed by a jacket of cooling water which surrounded the three tubular assemblies. Figure 5 depicts a cross-section of the generator module. The basic ozone generator configuration is shown in Figure 6.

Following ozone generation, the gas was collected at the exit end of the module and routed to the contact columns via a one-half inch (12.7 mm) stainless steel tube. Each of the contact columns had an inside diameter of 6 inches (15.2 cm). Made of stainless steel pipe and set on a steel base plate, each contact column was constructed of four flanged sections: two 6-ft (1.8 m) sections and two 2-ft (0.6 m) sections. Thus, each column totaled 16 feet (4.9 m) in height.

Ozonized air from the ozone generator was introduced at the bottom of the contact columns through porous stainless steel diffusers. Figures 7 and 8 show the rotameters and necessary piping that enabled the ozone to be split between the two columns. The off-gas from the top of the columns was vented to the treatment plant roof through Tygon tubing and released to the outside atmosphere.

Raw water was pumped from the treatment plant influent line through a flow meter and to the top of the first column using a one-half inch (12.7 mm) positive displacement pump powered by a 1-horsepower, variable-speed DC motor. The water then flowed down the first column, up to the top of the second column via a 2-inch (5.1 cm) PVC pipe, and

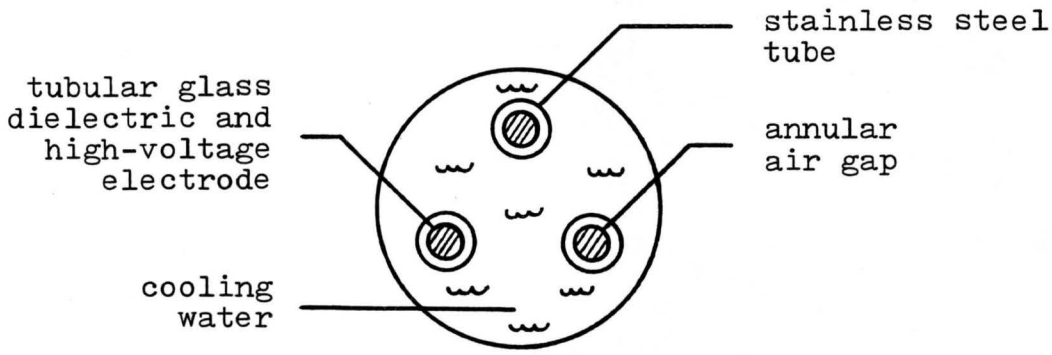


Figure 5. Ozone Generator Module
Cross-Section

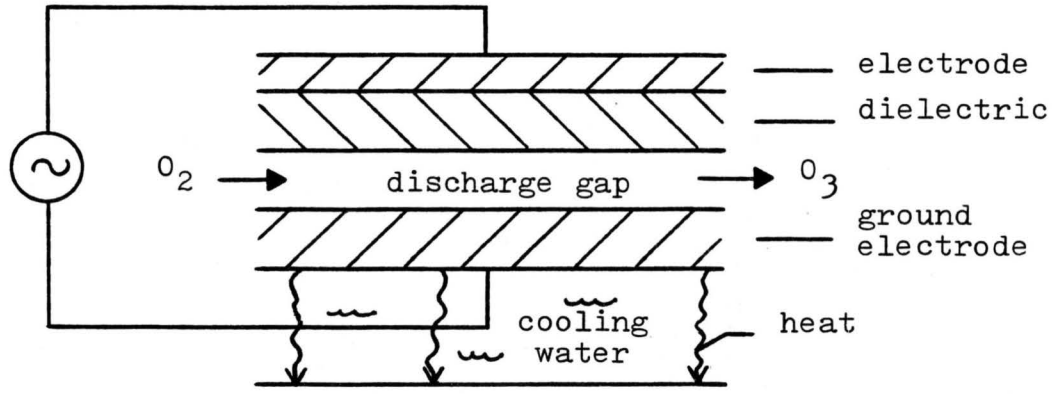


Figure 6. Ozone Generator Configuration

Figure 7. Contact Column Rotameters

Figure 8. Rotameters and Connecting Piping

down the second column. Thus, water and ozone flowed countercurrently in both columns. The effluent from the second column flowed into a constant-head tank and then to a nearby drain.

Experimental Procedures

Generator Production

To conserve valuable research time, the generator calibration curve developed by Stoebner (50) was approximated in lieu of recalibrating the generator at Huron. As Stoebner's literature review revealed, ozone production depends upon the type, quality, and flow rate of the feed gas; the temperature and pressure in the ozone generator; and the frequency and voltage of the power supply.

As with previous studies using this pilot plant, the feed-gas flow rate was held constant at 0.39 scfm (11 slpm), the ozone generator was maintained at a constant temperature of 68^{o}F (20^{o}C) and a constant pressure of 14 psig (97 kPa gage), and the power supply was a constant 60 Hz. Therefore, the ozone production of the generator was strictly a function of the applied voltage, which ranged from 0 to 20 kV as determined by the generator variac setting. At a setting of 0 per cent, no ozone was produced. At a setting of 100 per cent, an ozone concentration of 1 to 1.5 per cent was obtained. Depending upon the desired output, one to three dielectric tubes were used in the ozone generator during the course of the research.

As previously implied, ozone production is adversely affected by moisture in the feed-gas. Therefore, a dewpoint meter was used to

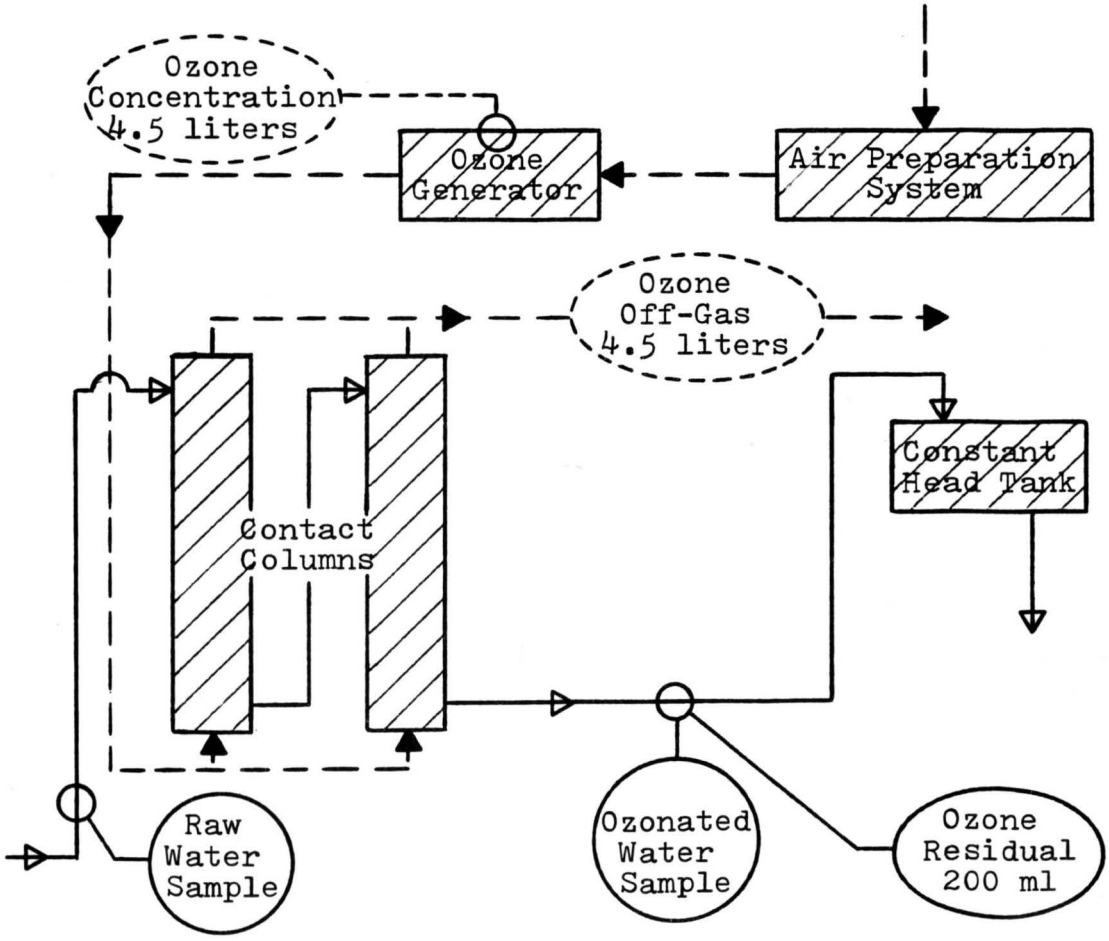
periodically determine the dewpoint of the feed-gas. In testing the feed-gas, an optimum dewpoint of -40°F (-40°C) was desired. However, this value was reached only when the pilot plant was operated daily for lengthy intervals. It is suspected that the desicant towers were more efficient when in frequent and continual operation.

Ozonized air was obtained from a Tygon sampling tube connected to the discharge port of the ozone generator. A schematic diagram of sampling locations and required sample volumes is detailed in Figure 9. The ozone concentration in the gas was determined using a variation of the iodometric method for measuring ozone residual as described in Standard Methods (47). Approximately 4.5 liters of the ozone-containing gas were passed at a rate of 1.5 liters per minute through a series of two gas washing bottles, each containing 400 ml of 1 per cent potassium iodide (KI) solution. The effluent tube of the second washing bottle was connected to a gas wet-test meter for measurement of the gas sample volume. The KI solution was then transferred to an erlenmeyer flask, acidified with 10 ml of 2 N sulfuric acid to a pH below 2, and titrated with 0.1 N sodium thiosulfate ($Na_2S_2O_3$) using a starch indicator solution.

The titration information along with the air flow rate was utilized to calculate the concentration of ozone in the air. A description of the calculations is presented in Appendix B.

Pilot Plant Operation

Operation of the pilot plant was based on the research of DeBoer (4):



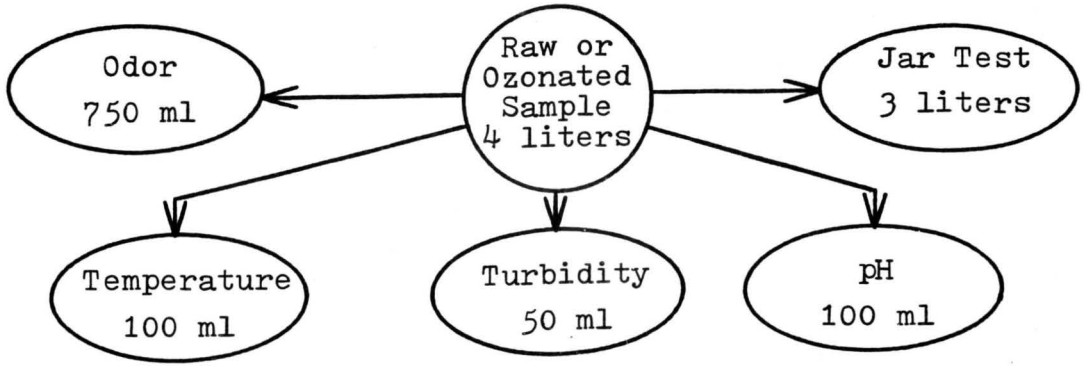


Figure 9. Schematic Flow and Sampling Diagram of the Ozone Pilot Plant

1) the liquid depth in the contact columns was 14.5 feet (4.4 meters)

2) the water and ozonized gas flowed countercurrently

3) the ozonized gas was proportioned so that approximately 64 per cent flowed through the first column while the remaining 36 per cent flowed through the second column

With all other variables being constant, column detention time and ozone dosage were the independent variables.

The column detention time is a function of the liquid volume and water flow rate. Because the liquid depth (and as a result, the liquid volume) was held constant, the detention time was a direct function of the water flow rate alone. Use of the positive displacement pump powered by a variable-speed motor enabled influent raw water flow rates of 1 gpm to 9 gpm (3.8 to 34.4 lpm) to be obtained. Since the contact columns had a constant water volume of 42.6 gal (163.0 liters), excluding the connecting piping, detention times of 5 to 40 minutes were easily obtainable.

The ozone concentration was a function of ozone generator power input and the air flow rate. An air flow rate of 0.39 scfm (11 slpm) was used, based on DeBoer's (4) research. Therefore, the concentration of ozone in the ozonized air became a function of the ozone generator power input alone.

The ozone concentration in the ozonized air, the air flow rate, and the water flow rate were the parameters of consideration in determining the applied ozone dosage. However, the air flow rate was constant. Therefore, the applied ozone dosage was totally dependent upon the generator power input and the water flow rate.

As alluded to in the above paragraph, the ozone concentration in the ozonized air was expressed as follows:

$$C = \frac{DV}{TQ} \qquad (11)$$

where: C = ozone concentration in contacting gas (mg/l)

D = applied ozone dosage (mg/l)

V = liquid volume in contact columns (liters)

T = contact column detention time (minutes)

Q = ozonized air flow rate (slpm)

Because the liquid volume in the contact columns and the ozonized air flow rate were held constant at 163 liters and 11 standard liters per minute, respectively, Equation 11 was simplified to:

$$C = 14.82\ D/T \qquad (12)$$

Thus, for any combination of ozone dosage and detention time, it was possible to calculate the required ozone concentration in the ozonized air which was then obtained by the generator variac setting.

Specific ozone dosages and column detention times relative to the ozone concentration in the ozonized air are presented in Table 3.

Transfer Efficiency and Ozone Residual

Transfer efficiency of the ozone as applied to the raw water was evaluated in this research. Ozone transfer efficiency was defined as follows:

$$E = 100\ (C - C_2)/C \qquad (13)$$

Where: E = transfer efficiency (%)

C = ozone concentration in the contacting gas (mg/l)

C_2 = ozone concentration in the off-gas (mg/l)

Table 3. Ozone Concentrations in Feed-Gas (C) Relative to Various Ozone Dosages and Contact Column Detention Times

Detention Time (T) (minutes)		5	10	15	20	30
Water Flow Rate (liters per minute)		32.6	16.3	10.9	8.2	5.4
Water Flow Rate (gallons per minute)		8.61	4.31	2.88	2.17	1.43
Pump Speed Setting (per cent of maximum)		85.0	46.5	33.7	27.2	20.0
Applied Ozone Dosage (D) (mg/l)	0	0	0	0	0	0
	4	11.9	5.9	4.0	3.0	2.0
	8	23.7	11.9	7.9	5.9	4.0
	12	N/A*	17.8	11.9	8.9	5.9
	16	N/A*	23.7	15.8	11.9	7.9
	24	N/A*	N/A*	23.7	17.8	11.9

$$C = 14.82\ D/T \quad (mg/l)$$

Note: Generator power settings were dependent upon the number of dielectric tubes used.

* Above maximum ozone generator output

During each of the pilot-plant operating runs, gas samples from the ozone generator and contact column off-gas were collected at the locations shown in Figure 9 and analyzed for ozone concentration. After the off-gas flow rate was measured, the analysis procedure for the ozone concentration in the off-gas was the same as that described previously under Generator Production.

The ozone residual in the contact column liquid effluent was also monitored during each operating run. The determination of ozone residuals was accomplished by back titration utilizing a Fischer and Porter amperometric titrator. The initial step involved the collection of a 200-ml sample in a 250-ml graduated cylinder containing 5 ml of 0.00564 N phenylarsine oxide (PAO) (47). Following this step, the sample was transferred to a 250-ml beaker after which 4 ml of acetate buffer and 1 ml of 5 per cent KI were added. The sample was then amperometrically titrated with 0.0282 N iodine which was standardized daily. The titration end-point was reached when a small increment of iodine solution caused a temporary deflection of the indicating pointer. A description of the calculations is presented in Appendix B.

Temperature and pH

During the flocculation enhancement studies, temperature and pH were monitored for the raw-water and ozonated raw-water samples and held constant for the jar-test samples. The temperature was measured with a mercury thermometer and pH with a Hach Model 2075 pH meter.

The temperatures of the jar-test samples were adjusted to $68^{o}F$ ($20^{o}C$) in the temperature-controlled laboratory. Sodium hydroxide or sulfuric acid was used to adjust the pH values to 8.4 units.

Odor Control

The effect of ozone on odor reduction, the major emphasis of this study, was evaluated using the Threshold Odor Test, detailed in Standard Methods (47). Odor tests were run on ozonated raw-water and corresponding raw-water samples. In addition, odor tests were run on samples collected from two treatment plant units, the presedimentation and solids contact basins, and on decanted jar-test samples. The relative position of the basins in the treatment plant is shown in Appendix E, Figure E1.

The decanted jar-test samples were analyzed for odor to determine the effect of various chemical combinations, both with and without pretreatment at an applied ozone dosage of 24 mg/l. The combinations tested are listed in Table 4 along with the appropriate chemical dosages that were used in both the treatment plant and jar tests. A detailed explanation of the jar-test procedure is given in the following section, Flocculation Studies.

Samples to be tested for odor intensity were initially collected in glass-stoppered 500-ml erlenmeyer flasks which were filled to the top and stored overnight at $4^{o}C$ for testing the following day.

The Threshold Odor Test, based on a method of limits, was used to obtain qualitative descriptions and approximate quantitative measurements of odor intensity. Because the testing "device" was the fallible human nose, care was taken in selecting six panelists who not only had an interest in the research but also had fairly sensitive noses. Because personal habits such as eating, smoking, and washing can have a profound effect on sensitivity to odors, the panelists were requested

Table 4. Decanted Jar-Test Odor Samples

Water Status	Jar Test Chemicals	Dosage (mg/l)
Raw	Potassium Permanganate ($KMnO_4$)	3
Raw	Activated Carbon (A.C.)	12
Raw	$KMnO_4$ + A.C.	
Raw	Coagulant Chemicals:	
	Polyelectrolyte (Nalco #8102)	1.4
	Alum	22
	Sodium Aluminate (Nalco #2)	15
	Polyelectrolyte (Nalco #8184)	0.3
Raw	All Chemicals:	
	Potassium Permanganate	
	Activated Carbon	
	Coagulant Chemicals	
Ozonated Raw (24 mg/l)	Coagulant Chemicals	

not to eat immediately before participating in an odor panel. Non-smokers were chosen. An odorless soap and odor-free water were available for washing.

Odor-free water was obtained by filtering demineralized water through activated carbon. Specific sample volumes were then diluted with odor-free water to a total volume of 200 ml in glass-stoppered 500-ml erlenmeyer flasks. These dilutions were then heated in a constant-temperature water bath to the threshold test temperature of 60 ± 1°C for evaluation by the panelists.

At least five panelists and six different dilutions were used for each test. The panelists were asked to compare each dilution with an odor-free blank for the presence or absence of odor. The threshold odor number was calculated for the lowest dilution for which an odor was detected. Using the total volume of 200 ml, each individual threshold odor number (TON) was then defined as follows:

$$TON = 200/(\text{ml of sample}) \qquad (14)$$

Table 5 contains threshold odor numbers corresponding to various dilutions as found in Standard Methods (47).

Because of the human factor, anomalous responses sometimes occurred. For example, a low concentration was called positive (having an odor) while a higher concentration was called negative (lacking an odor). In such cases, the threshold was designated at the point of detection after which no further anomalies occurred. The threshold of the panel as a whole was defined as the geometric mean of the individual threshold odor numbers. Appendix B contains the necessary calculations.

Table 5. TON Values of Various Dilutions (47)

Sample Volume (ml)	TON	Sample Volume (ml)	TON
200	1	12	17
140	1.4	8.3	24
100	2	5.7	35
70	3	4	50
50	4	2.8	70
35	6	2	100
25	8	1.4	140
17	12	1.0	200

For statistical purposes, the raw mean of the individual threshold odor numbers was also computed.

Flocculation Studies

A revised standard procedure of the jar test (18) was used in the flocculation studies. A total of six 1-liter samples were collected for each run. Three of the samples were raw water and the other three were ozonated raw water. Constant average dosages of the coagulant chemicals used at the Huron plant were added to each of the samples. The coagulant chemicals are listed in Table 4.

Following stirring and sedimentation, decanted samples were drawn from the jars and analyzed for turbidity. Because temperature and pH were constant, the turbidity values were assumed to be a direct function of the flocculation efficiency. Thus, it was assumed that the flocculation process was more efficient for the sample with the lowest average turbidity. In addition to the turbidity values, visual observations were also noted.

Besides studying the effect of the coagulant chemicals only, jar tests were also utilized during the optimum run to analyze the effectiveness of adding all of the chemicals presently used at the Huron plant through the solids contact basin. The chemicals and dosages are tabulated in Table 4. The locations of chemical additions are shown in Appendix E, Figure E1.

The jar-test procedure follows. Each sample was collected in a 1,000-ml graduated cylinder and transferred to a square (4.5-in x 4.5-in x 6-in), wide-mouth, 2-liter capacity, glass jar. The jars were

then placed in their appropriate location on a six-paddle jar test apparatus which was equipped with retractable paddles. Initially, the paddles were placed in the samples at a depth of half the sample depth (1.5 inches) and started at 150 revolutions per minute (rpm). Immediately, chemical reagents were pipetted from their respective stock solutions and into the samples in the same order as in plant practice. Depending on the test purpose, the following additions were made: potassium permanganate (optional), activated carbon (optional), alum, and a polyelectrolyte (Nalco #8102). Rapid mixing was continued for 1.5 minutes, after which the paddles were stopped and retracted from the samples. A 10-minute quiescent period was allowed for floc formation. This part of the test represented the flash mix and flocculation basin treatment that occurs in the plant.

To simulate the solids contact basin which followed the flocculation basin, the paddles were again placed in the samples and rotated at 150 rpm. Lime was quickly added to the samples, which were agitated at 150 rpm for an additional 1.5 minutes. Finally, sodium aluminate (Nalco #2) and a polyelectrolyte (Nalco #8184) were added, while mixing continued for an additional 1.5 minutes. Paddle speed was then reduced to 40 rpm for 3 minutes. The paddles were finally stopped and removed from the samples, allowing floc to form and settle for 15 minutes.

At this juncture, 40 ml were removed with a "wide mouth" pipette from each sample at a point half the depth of the samples in the jars (1.5 inches) and tested for turbidity. The instrument used to measure turbidity was a Hach Model 2100A turbidimeter. Calibration of the

instrument was based on Formazin, and the unit of measure was the Nephelometric Turbidity Unit (NTU). Because stray light was only significant in the 0 NTU to 0.2 NTU range, research results were not affected.

RESULTS AND DISCUSSION

Transfer Efficiency and Ozone Residual

The ozone contacting efficiencies and residuals from Appendix C, Table C2, are summarized in Table 6. It is evident that the transfer efficiencies ranged from 80 to 92 per cent. It would appear that these efficiencies did not vary with ozone dosage. For example, the average transfer efficiencies computed for the 4 and 24 mg/l dosages were 91 and 89 per cent, respectively. These results are contrary to the results anticipated from the work of DeBoer (4) and Stoebner (50), who found that transfer efficiency decreased with increasing ozone dosages. According to these researchers, a possible explanation for their observations was that at higher dosages, a greater portion of the ozone demand was satisfied causing the remaining ozone to be released as off-gas. Their research was conducted on a groundwater. However, it is quite possible that in surface waters having a high organic content, as encountered at Huron, the ozone demand remained high and as a result was not a factor affecting transfer efficiency. If this were the case, the contacting efficiency of the ozone would be expected to remain relatively constant. Also shown in Table 6, the ozone residuals ranged from 0 to 0.82 mg/l. These values were much lower than those reported by DeBoer (4) and Stoebner (50), a fact again attributable to the poor quality of the raw surface water at Huron. The ozone residuals showed a general trend of increasing with the dosage, as was expected. Ozone residuals were not detected until the dosage was increased to 12 mg/l.

Table 6. Summary of Ozone Analyses

Applied Ozone Dosage (mg/l)	Testing Date (1981)	Ozone Residual (mg/l)	Absorbed Ozone Dosage (mg/l)	Ozone Demand (mg/l)	Contacting Efficiency (per cent)
4	6/22	0	3.42	3.42	92
	7/8	0	3.61	3.61	90
8	6/25	0	7.22	7.22	85
	7/8	0	7.30	7.30	85
12	6/19	0.30	10.17	9.87	90
	7/13	0.09	11.91	11.82	91
16	6/18	0.82	12.25	11.43	83
	7/13	0.38	13.08	12.70	80
24	6/24	0.69	20.30	19.61	84
	7/6	0.66	19.86	19.20	91
24 Optimum	7/16	0.71	20.83	20.12	91

However, it should be noted that the highest ozone residual, 0.82 mg/l, occurred at the 16 rather than the 24 mg/l applied ozone dosage. This result might have occurred due to a marked deterioration in raw water quality that developed due to the no-flow condition in the river after June 18, the date of the 0.82 mg/l residual.

Temperature and pH

The temperature and pH data collected for the raw- and ozonated raw-water samples during the flocculation enhancement study are tabulated in Appendix C, Table C3, and presented in Table 7. It can be seen from this table that although the water temperature remained constant during ozonation on any given day, the raw-water temperature did vary from 20°C on June 18, 1981, to 29°C on July 13, 1981. Also from the table, it would appear that ozonation did have an effect on pH at the 16 and 24 mg/l dosages, where decreases of 0.2 and 0.3 units, respectively, were recorded. Such changes were not observed at the lower dosages. A possible explanation for the pH decrease involves the tendency of ozone to react with hydroxyl ions, as noted in the LITERATURE REVIEW (39). Based on this premise, the reaction of hydroxyl ions with ozone at the higher concentrations would reduce the hydroxyl ion concentration and thereby lower the pH of the water.

Odor Control

The results of the analyses conducted to determine the influence of ozonation on the odor of the Huron water supply are summarized in Table 8. The raw data may be found in Appendix C, Table C4. It is assumed

Table 7. Summary of Temperature and pH Data

Applied Ozone Dosage (mg/l)	Testing Date (1981)	Temperature (°C)		pH (Units)	
		Raw	Ozonated	Raw	Ozonated
0	6/19	20	20	8.4	8.4
	7/1	26	26	8.5	8.5
4	6/22	22	22	8.4	8.4
	7/8	24		8.5	
8	6/25	23	23	8.3	8.3
	7/8	24		8.5	
12	6/19	20	20	8.4	8.4
	7/13	29		8.6	
16	6/18	20	20	8.4	8.2
	7/13	29		8.6	
24	6/24	23	23	8.4	8.1
	7/6	26		8.5	
24 (Optimum)	7/16	27	27	8.6	8.3

Table 8. Summary of Threshold Odor Test Results

Water Sample	Collection Date (1981)	Panel TON		General Characteristic Odor
		Geometric Mean	Raw Mean	
Raw	7/1	9.6	10.1	Fishy
Ozonated Raw (0 mg/l)	7/1	11.6	12.1	Fishy
Raw	7/8	22.7	22.9	Fishy
Ozonated Raw (4 mg/l)	7/8	15.8	16.3	Sweeter
Raw	7/8	24.1	24.1	Fishy
Ozonated Raw (8 mg/l)	7/8	18.8	19.2	Sweet
Raw	7/13	15.8	16.3	Fishy
Ozonated Raw (12 mg/l)	7/13	24.1	24.7	Sweet
Raw	7/13	16.7	18.1	Musty
Ozonated Raw (16 mg/l)	7/13	13.2	13.4	Sweet
Raw	7/6	20.1	20.8	Fishy
Ozonated Raw (24 mg/l)	7/6	5.4	6.2	Sweet
Presed. Basin Eff.	7/6	21.4	22.8	Musty
Solids Contact Eff.	7/6	11.8	11.8	Fishy
Raw	6/29	7.6	7.9	Fishy
Raw + Activated Carbon	6/29	9.2	10.8	Fishy
Raw + $KMnO_4$	6/29	10.3	10.7	Fishy
Raw + Act. Car. + $KMnO_4$	6/29	10.3	10.5	Fishy
Raw	7/16	40.3	43.1	Fishy
Raw + Coag. Chem.	7/16	26.2	28.2	Fishy
Raw + All Chem.	7/16	18.0	18.2	Fishy
Ozonated Raw (24 mg/l)	7/16	15.6	16.2	Sweet
Ozonated + Coag. Chem.	7/16	14.5	14.7	Sweet

that Huron's odor problem originates from natural sources such as vegetation decomposition and algae. Although it appears from Appendix C, Table C3, that the general water quality of the James River remained relatively constant during the study in terms of organic content, the data tabulated in Table 8 indicates that the odor level did not. An important point must be emphasized when considering the odor data. The panelists consistently described the odor of the raw water as being fishy, unpleasant, harsh, or gross. On the other hand, the ozonated samples were characterized as being sweet-smelling rather than unpleasant. Thus, it was possible for a raw-water sample with a low TON to have an unpleasant odor while an ozonated sample of raw water with a higher TON had a pleasant odor. This fact must be considered when evaluating Threshold Odor Test data.

When the raw-water Threshold Odor Numbers (TON) were plotted versus time (Figure 10), it was evident that the odor intensity of the raw water increased during the research period as the water became more and more stagnant due to a no-flow situation that existed in the river. The TON of the raw water climbed from approximately 7 in late June to more than 40 in mid July. The dip in the curve (July 13) can probably be attributed to a small amount of rainfall that occurred between July 8 and July 16.

A general picture of the raw- and ozonated raw-water TON's is presented in Figure 11. At a 0 mg/l applied ozone dosage (aeration only), the TON's were approximately equal. At 4 and 8 mg/l dosages, there appears to be an odor intensity reduction due to ozonation. At 12

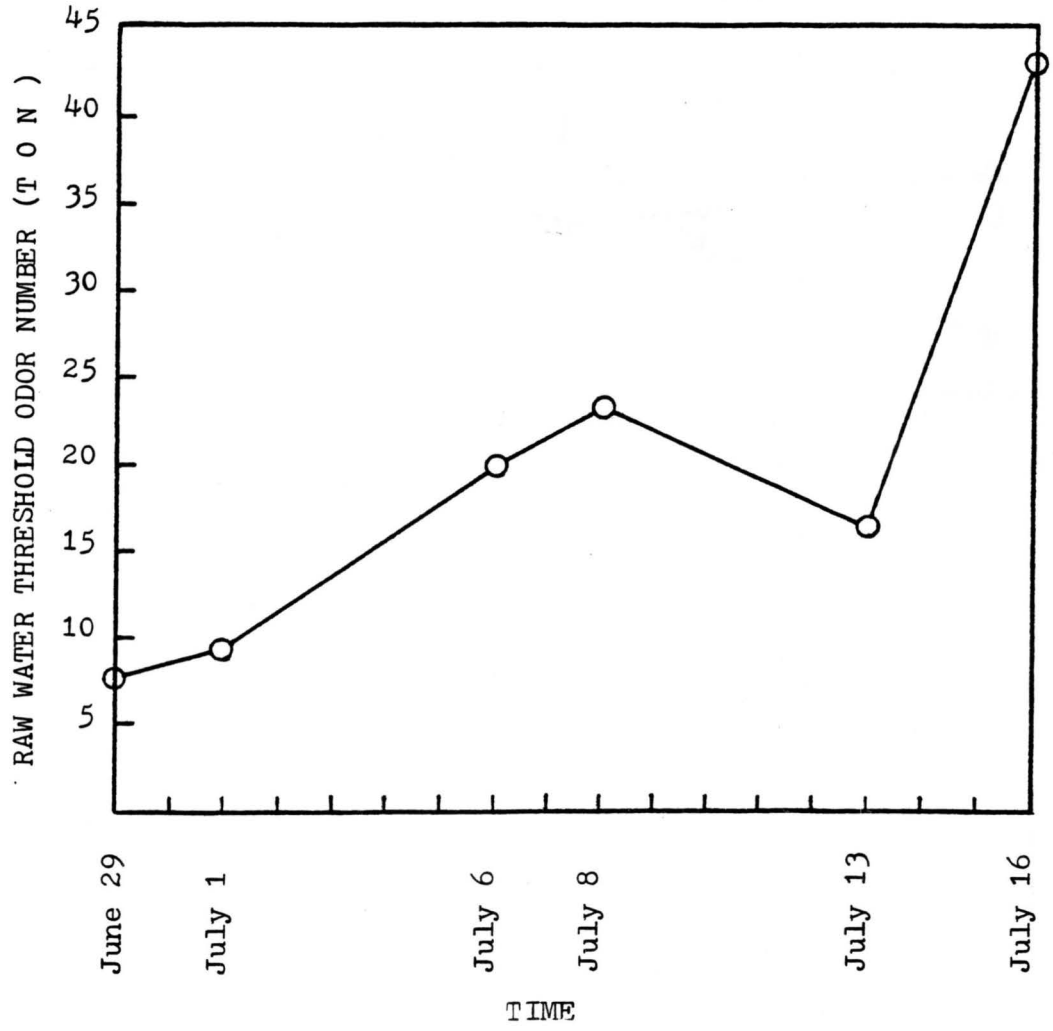


Figure 10. Raw Water TON versus Time

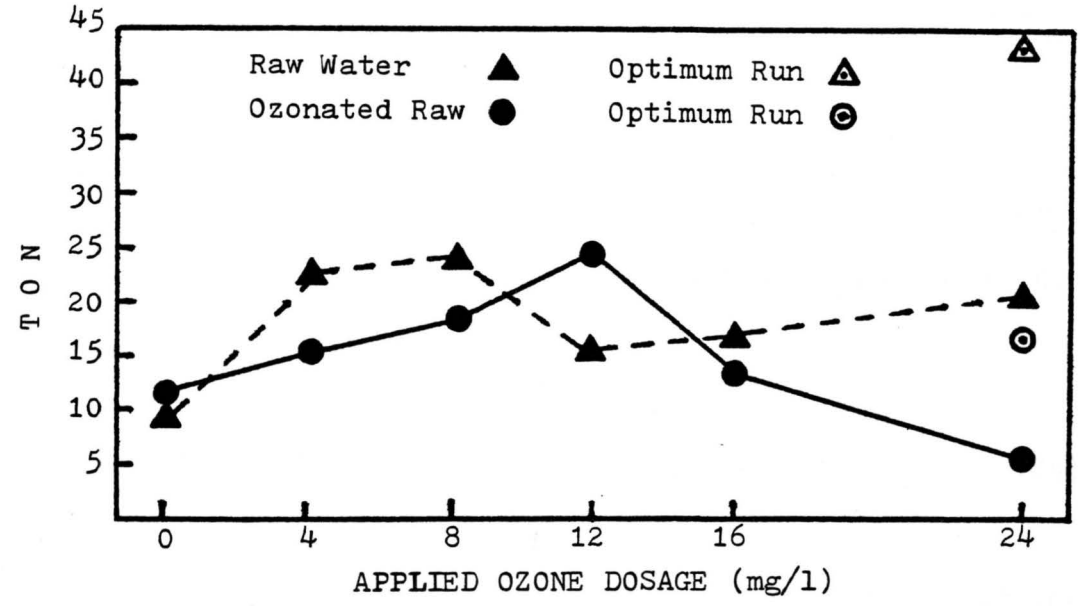


Figure 11. TON versus Ozone Dosage

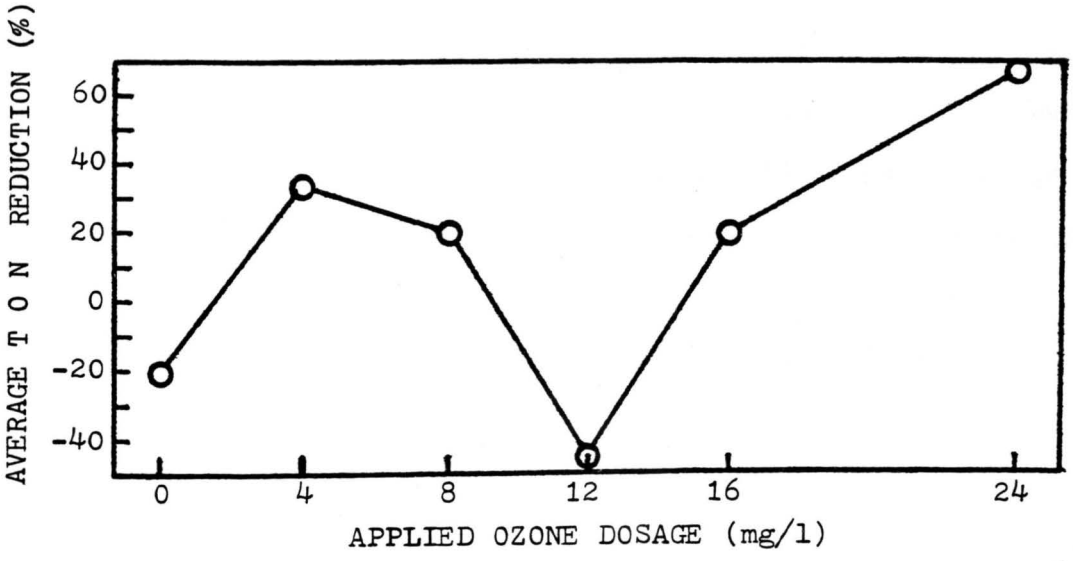


Figure 12. TON Reduction versus Ozone Dosage

mg/l, the ozonated raw water had a higher TON than the raw water. The 16 mg/l run resulted in no major change in odor intensity. However, at the 24 mg/l dosage, ozonation produced a major reduction in the odor intensity of the raw water.

In Figure 12, the average odor reduction is plotted against the applied ozone dosage. As seen, the curve dips to a negative reduction in odor intensity at the 12 mg/l dosage and climbs to a 60 per cent reduction at the 24 mg/l dosage.

The odor data were statistically analyzed using computerized Analysis of Variance (ANOVA) and Waller-Duncan k-ratio t Test (49) procedures.

ANOVA was used to detect differences due to treatments at the 99 per cent confidence level and is summarized for each testing date in the following ANOVA tables. In the procedure, which is essentially an arithmetic process that recognizes sources of known variation and tests for equality of means, computed variance ratios (denoted by F) were compared to tabular F values. Thus, if a computed F value was greater than the appropriate tabular F value at the 99 per cent confidence level, a statistical difference (denoted by **) was present.

Because ANOVA cannot detect specific differences when more than two treatments are analyzed, individual treatments were analyzed with the Waller-Duncan k-ratio t Test at a k ratio of 100:1 (95 per cent confidence level). In this test, a t table was entered on the basis of the treatment F values. The test, which utilized raw means of the individual TON values rather than the standard geometric means, was interpreted as follows.

The raw means of individual TON values were placed in groupings. If sample means from each testing date were placed in the same letter grouping, their threshold odors were not significantly different. For example, if both raw- and ozonated raw-water samples were placed in group A, their threshold odors were not different at the 95 per cent confidence level. However, if the raw sample was placed in group A and the ozonated sample in group B, the sample threshold odors were designated as different.

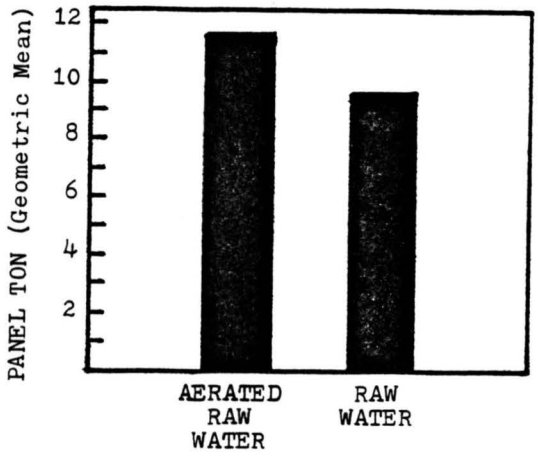
The ANOVA results are shown in Tables 9 through 14 and the Waller-Duncan test results are tabulated in Figures 13 through 18, which also contain bar graphs of the corresponding panel TON values (geometric means). It should be noted that each set of odor data is the result of a given day of testing, as indicated in Table 8.

As the F values in Table 9 indicate, no statistical difference was found in TON's between the raw- and aerated raw-water samples. The bar

Table 9. ANOVA Procedure for TON of Raw and Ozonated Raw Water (0 mg/l, Aeration Only), 7/1/81

Source	Degrees of Freedom	Mean Square	F
Treatment	1	3.71	0.36
Observer	5	14.73	1.44
Residual	4	10.24	

graph in Figure 13 graphically shows the two TON values obtained from the odor tests. From the graph it would appear that the two values are



GROUPING*	MEAN OF INDIVIDUAL T O N	NUMBER OF PANELISTS	ODOR SAMPLE
A	12.1	6	AERATED RAW WATER
A	10.1	6	RAW WATER

NOTE: *TON's with same letter are not significantly different at the 5% level.

Figure 13. TON Analysis of Raw and Ozonated Raw Water (0 mg/l, Aeration Only), 7/1/81

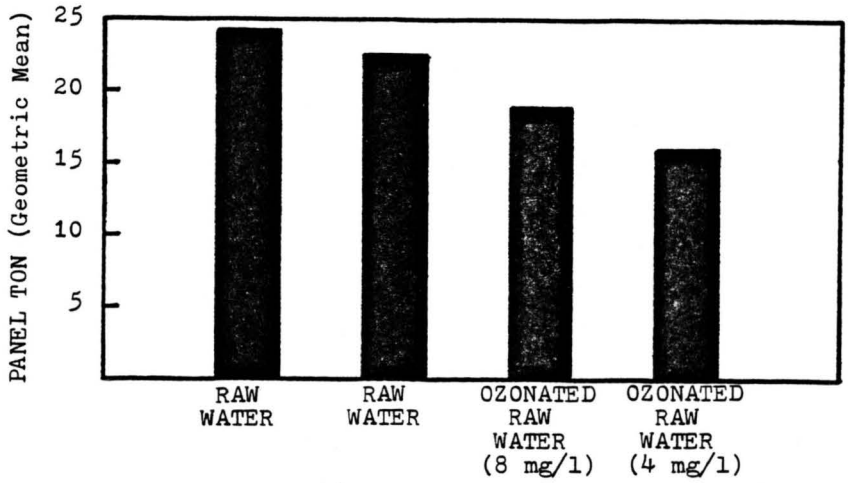
different. However, a review of the tabulation in Figure 13 substantiates that no statistical difference in TON's exists between the raw- and aerated raw-water samples. As seen, the aerated raw water had a mean of individual TON's equal to 12.1 and was placed in group 'A'. The raw water had a mean of individual TON's equal to 10.1. However, because of the variability existing in the odor test, the raw water was also placed in group 'A'. As indicated by the note below the table, "TON's with the same letter are not significantly different at the 5 per cent level."

In Table 10, the ANOVA results show a significant TON difference

Table 10. ANOVA Procedure for TON of Raw and Ozonated Raw Water (4 and 8 mg/l), 7/8/81

Source	Degrees of Freedom	Mean Square	F
Treatment	3	76.42	8.94**
Observer	5	18.76	2.19
Residual	15	8.55	

due to treatment for the samples collected on July 8, 1981. The TON values from the 4 and 8 mg/l runs are shown graphically in Figure 14. Reference to the table in this figure indicates no significant odor difference between the two ozonated samples. However, a significant odor reduction was detected between the raw-water samples and the ozonated raw-water samples, as confirmed by the appropriate letters in the grouping column. Thus, an applied ozone dosage of 4 or 8 mg/l is probably adequate for most odor applications at Huron.



GROUPING*	MEAN OF INDIVIDUAL T O N	NUMBER OF PANELISTS	ODOR SAMPLE
A	24.1	6	RAW WATER
A	22.9	6	RAW WATER
B	19.1	6	OZONATED RAW WATER (8 mg/l)
B	16.3	6	OZONATED RAW WATER (4 mg/l)

NOTE: *TON's with same letter are not significantly different at the 5% level.

Figure 14. TON Analysis of Raw and Ozonated Raw Water (4 and 8 mg/l), 7/8/81

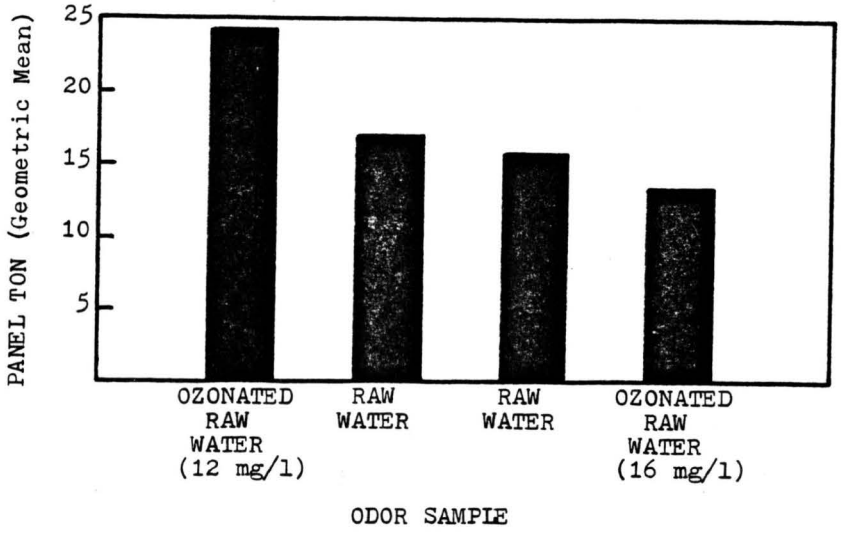
The ANOVA results shown in Table 11 also indicate a significant TON difference due to treatment for the July 13, 1981, odor samples. The

Table 11. ANOVA Procedure for TON of Raw and Ozonated Raw Water (12 and 16 mg/l), 7/13/81

Source	Degrees of Freedom	Mean Square	F
Treatment	3	137.87	6.67**
Observer	5	50.17	2.43
Residual	15	10.66	

12 and 16 mg/l run results are graphed relative to the respective raw-water TON's in Figure 15. As previously noted, the 12 mg/l ozone dosage resulted in a sample TON higher than that of the raw water. This fact is confirmed in the table in Figure 15. Even though the sample ozonated at a dosage of 12 mg/l had a significantly higher TON, the sample was characterized as having a "sweet" odor (Table 8). The sample ozonated at a dosage of 16 mg/l was similarly characterized, although the table in Figure 15 indicates that the odor intensity of the raw and ozonated samples was not different.

A significant TON difference due to treatment was indicated by the ANOVA procedure for the July 6, 1981, water samples. As Table 12 shows, the significant odor difference was again due to the treatment only and not the individual observations.



GROUPING*	MEAN OF INDIVIDUAL T O N	NUMBER OF PANELISTS	ODOR SAMPLE
A	24.7	6	OZONATED RAW WATER (12 mg/l)
B	18.1	6	RAW WATER
B	16.3	6	RAW WATER
B	13.4	6	OZONATED RAW WATER (16 mg/l)

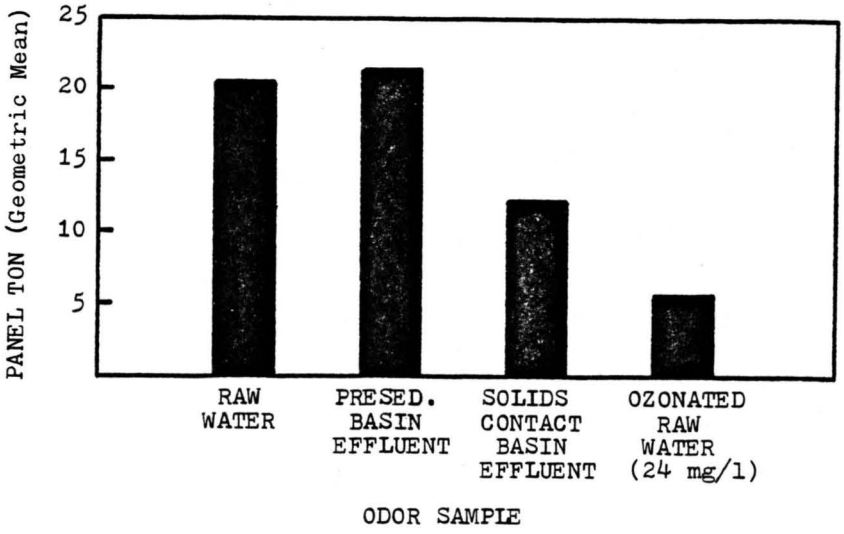
NOTE: *TON's with same letter are not significantly different at the 5% level.

Figure 15. TON Analysis of Raw and Ozonated Raw Water (12 and 16 mg/l), 7/13/81

Table 12. ANOVA Procedure for TON of Raw and Ozonated Raw Water (24 mg/l), Presedimentation Basin Effluent, and Solids Contact Basin Effluent, 7/6/81

Source	Degrees of Freedom	Mean Square	F
Treatment	3	365.87	12.56**
Observer	5	42.94	1.47
Residual	15	29.13	

The results of the 24 mg/l run are graphed in Figure 16. Also included are the results of the odor tests on the raw water, presedimentation basin effluent, and solids contact basin effluent. Reference to the table in Figure 16 indicates that ozonation at 24 mg/l significantly reduced the odor intensity of the raw water. The table also shows no significant difference in odor between the raw-water sample and the presedimentation basin sample (which was treated with potassium permanganate and activated carbon). Statistically, the table reveals a difference in odor intensity between the raw-water and the solids contact basin effluent samples. However, no significant difference was found between the ozonated raw-water sample and the solids contact basin effluent. The odor intensity reduction in the solids contact basin was probably due to the coagulation, flocculation, and sedimentation processes which occurred in the basin. On the other hand, the odor reduction resulting from the 24 mg/l applied ozone dosage was due to ozonation alone.



GROUPING*	MEAN OF INDIVIDUAL T O N	NUMBER OF PANELISTS	ODOR SAMPLE
A	22.8	6	PRESED. BASIN EFFLUENT
A	20.8	6	RAW WATER
B	11.8	6	SOLIDS CONTACT BASIN EFFLUENT
B	6.2	6	OZONATED RAW WATER

NOTE: *TON's with same letter are not significantly different at the 5% level.

Figure 16. TON Analysis of Raw and Ozonated Raw Water (24 mg/l), Presedimentation Basin Effluent, and Solids Contact Basin Effluent, 7/6/81

Because activated carbon and potassium permanganate are both used at Huron to combat odor, raw-water samples were dosed with these chemicals in various combinations, allowed to react at plant temperature for approximately two hours, stored at $4^{o}C$ overnight, and tested for odor the following day. The ANOVA results shown in Table 13 show that

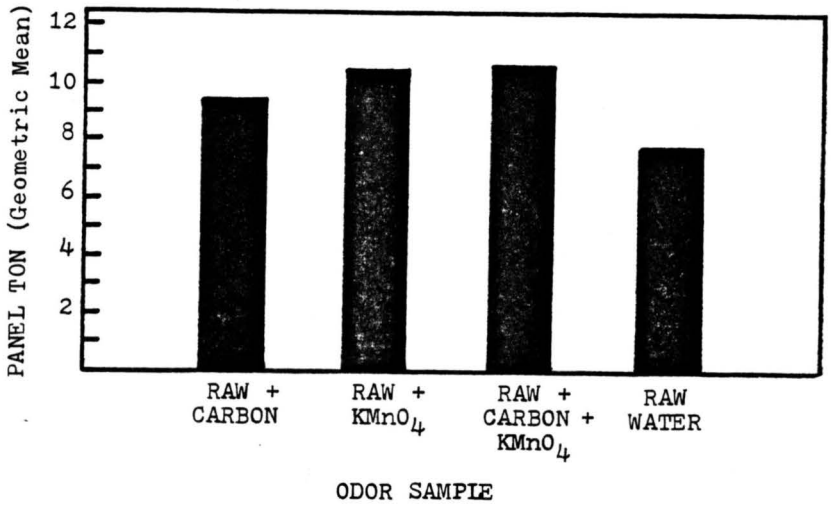
Table 13. ANOVA Procedure for TON of Raw- and Treated-Water Samples, 6/29/81

Source	Degrees of Freedom	Mean Square	F
Treatment	3	11.86	0.73
Observer	5	23.39	1.45
Residual	15	16.18	

the TON values for the raw- and treated-water samples were not significantly different.

The odor results of the specific chemical additions are shown in Figure 17. As Table 4 indicates, the carbon and potassium permanganate dosages were 12 and 3 mg/l, respectively. Figure 17 shows that these chemicals, whether added singly or in combination, caused no significant change in the raw-water TON at these dosages.

Because the 24 mg/l applied ozone dosage resulted in a substantial odor reduction, this run was repeated. In addition, odor tests were also run on jar-test samples which had been subjected to various treatment plant processes. Table 14 indicates a significant TON difference due to treatment for the optimum run samples.



GROUPING*	MEAN OF INDIVIDUAL T O N	NUMBER OF PANELISTS	ODOR SAMPLE
A	10.8	6	RAW + CARBON
A	10.7	6	RAW + $KMnO_4$
A	10.5	6	RAW + CARBON + $KMnO_4$
A	7.9	6	RAW WATER

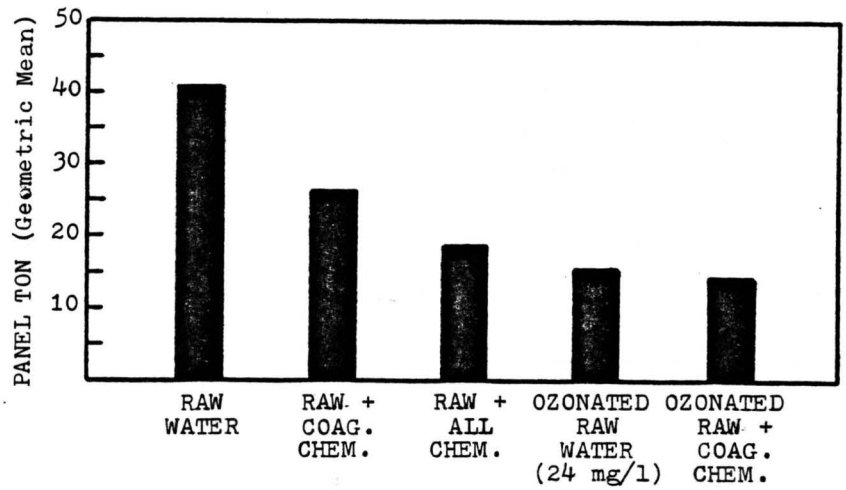
NOTE: *TON's with same letter are not significantly different at the 5% level.

Figure 17. TON Analysis of Raw- and Treated-Water Samples, 6/29/81

Table 14. ANOVA Procedure for Optimum Run TON Values, 7/16/81

Source	Degrees of Freedom	Mean Square	F
Treatment	4	707.17	8.02**
Observer	4	133.54	1.52
Residual	16	88.14	

Specific optimum run odor results are graphed in Figure 18. The raw water was very odorous, probably due to a major algae bloom, and had a TON of 43. The table in Figure 18 indicates that significant odor reductions occurred due to the various treatments. As seen, odor intensities were significantly reduced when the raw water was treated with either ozone or chemicals (comparing the A grouping with the B and C groupings). However, there was no significant difference in odor intensities between raw water treated with ozone and raw water treated with the plant chemicals (up through the solids contact basin). In fact, the raw water treated with all chemicals, ozonated raw water, and ozonated raw water plus coagulant chemicals were all placed in the same odor level group, group C. At this juncture, an important point must again be stressed. All of the unozonated samples exhibited unpleasant, fishy odors, as noted in Table 8. On the other hand, the panelists reported that the ozonated samples had a pleasant, sweet odor. This characteristic difference should be given equal, if not greater, emphasis relative to odor intensity (TON) when determining the palatability of a drinking water.



GROUPING*	MEAN OF INDIVIDUAL T O N	NUMBER OF PANELISTS	ODOR SAMPLE
A	43.1	5	RAW WATER
B	28.2	5	RAW WATER + COAG. CHEM. (Jar Test)
C B	18.2	5	RAW WATER + ALL CHEM. (Jar Test)
C B	16.2	5	OZONATED RAW WATER
C	14.7	5	OZONATED RAW WATER + COAG. CHEM. (Jar Test)

NOTE: *TON's with same letter are not significantly different at the 5% level.

Figure 18. TON Analysis of Optimum Run Samples, 7/16/81

Flocculation Studies

Studies were also conducted to evaluate the effect of ozonation on flocculation using the jar-test procedure. Jar tests were run on raw and ozonated water, both treated with the coagulant chemicals. Flocculation efficiencies were evaluated by comparing the turbidities of the settled jar-test samples. The results of these tests may be found in Table 15.

Figure 19 is a plot of the raw-water turbidity values. As shown, turbidities ranged from 19 to 35 NTU's over the 4-week test period, although it is suspected that the 35-NTU value was possibly the result of a non-representative "slug" flow in the river. Figure 19 also depicts the turbidity values of the corresponding ozonated raw-water samples. The values appear inconsistent because they vary from slightly lower to much higher than those measured in the corresponding raw-water samples. The higher turbidities were expected, especially at higher ozone dosages, because increased turbidity is a documented effect of ozonation (45).

Two sets of jar-test results were statistically analyzed using the Analysis of Variance (ANOVA) procedure (49). Tables 16 and 17 contain the ANOVA information for the raw water treated with coagulant chemicals and the ozonated raw water treated with coagulant chemicals, respectively. Again, the ANOVA procedure (and resulting F value) was carried out at the 99 per cent confidence level.

Table 15. Flocculation Study Results

(1)	(2)	(3)	(4)	(5)	(6)	(7)
Applied Ozone Dosage (mg/l)	Testing Date (1981)	Sample Turbidity Values (NTU's)				
		Raw Water	Ozonated Raw Water	Raw + All Chem. (Jar Test)	Raw + Coag. Chem. (Jar Test)	Ozonated + Coag. Chem. (Jar Test)
0 Aerated	6/19	19	19	1.4 1.6 (1.8) 2.3	4.1 1.4 (2.3) 1.3	3.4 3.5 (3.9) 4.7
	6/23	35	43	0.81	1.1 1.1 (1.1) 1.1	0.88 0.82 (0.85) 0.86
	6/24*	20	18		1.8 1.8 (1.9) 2.0	0.75 0.79 (0.77) 0.78
4	6/22	24	22	3.5 4.2 (3.7) 3.5	17 24 (22) 24	
	6/22*	24	22		2.2 3.4 (3.0) 3.4	1.5 1.8 (1.8) 2.2
8	6/25	29	29 25 (27) 27		2.1 2.8 (2.3) 2.1	1.6 1.6 (1.5) 1.4
12	6/19	19	17		20 22 (22) 25	3.2 3.2 (3.4) 3.8
16	6/18	21	25	27 22 (25) 25	11.0 9.0 (8.2) 4.5	1.1 1.3 (1.3) 1.4
24	6/24	20	18		1.8 1.8 (1.9) 2.0	5.3 5.5 (5.4) 5.4
24 Optimum	7/16	23 28 (27) 29	53	0.85 1.0 1.1 (1.0) 1.2 1.0	1.8 1.8 1.8 (1.9) 2.0 2.0 2.0	0.95 1.4 1.4 (1.2) 1.3 0.94 0.96

Note: ( ) Indicates Sample Mean

* Indicates Value Selections Plotted

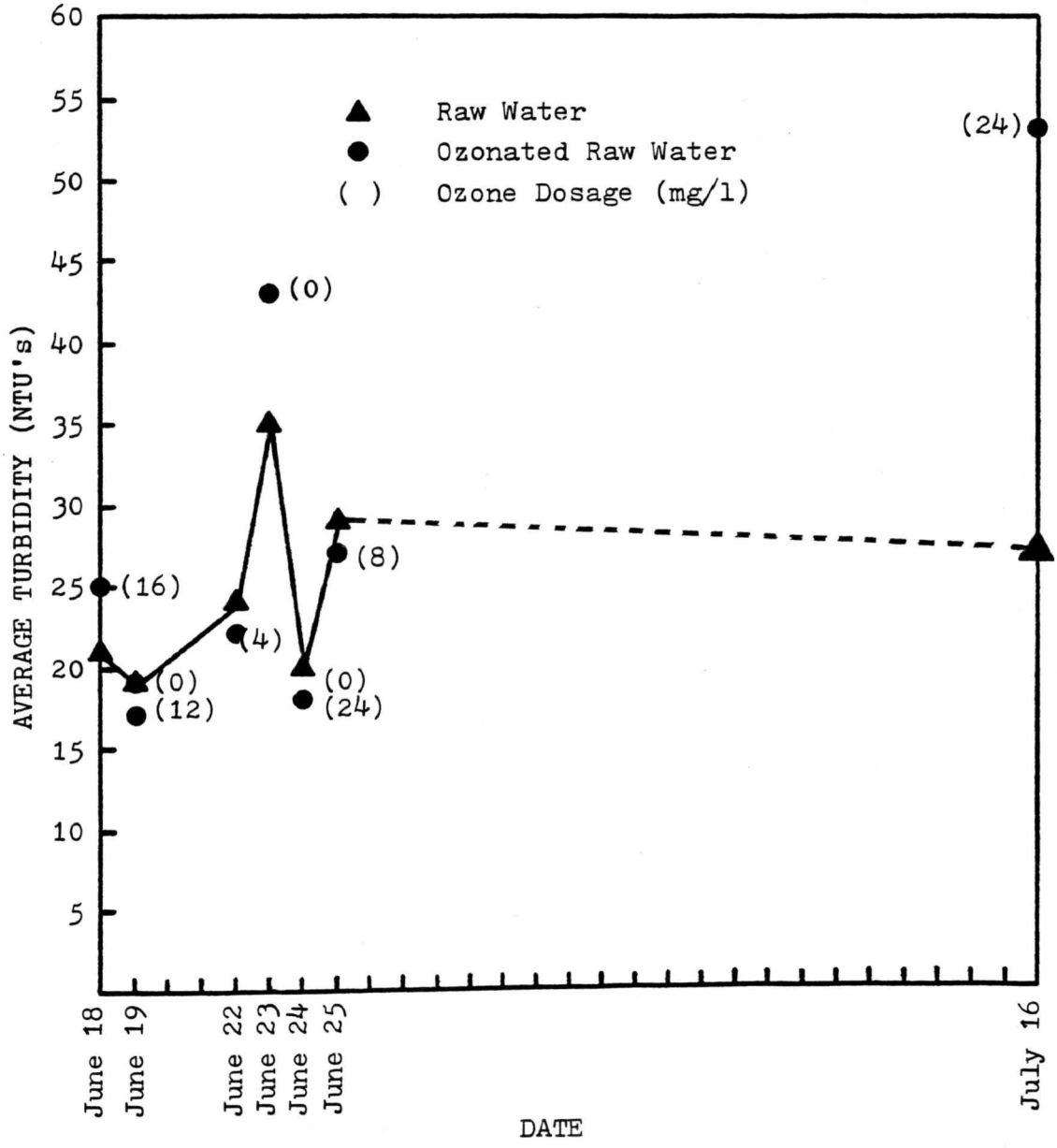


Figure 19. Raw-Water and Corresponding Ozonated Raw-Water Turbidity Values

Table 16. ANOVA Procedure for Raw-Water Settled Jar-Test Samples

Source	Degrees of Freedom	Mean Square	F
Dose	5	224.15	116.68**
Date (Dose)	2	0.59	0.31
Residual	22	1.92	

There were 30 corresponding pairs of turbidity observations reported in Table 15 (Columns 6 and 7) for the raw and ozonated raw water with coagulant chemicals. As a result, 30 data points were used

Table 17. ANOVA Procedure for Ozonated Raw-Water Settled Jar-Test Samples

Source	Degrees of Freedom	Mean Square	F
Dose	5	3.23	0.12
Date (Dose)	2	27.31	315.23**
Residual	22	0.87	

in each of the ANOVA procedures, Tables 16 and 17.

Examination of Table 16 reveals a significant difference in the jar-test turbidities of raw water treated with coagulant chemicals (Table 15, Column 6) corresponding to the various ozone dosages. Thus, while a difference in turbidity values was exhibited for the raw-water jar tests (Column 6) in Table 15, there was no statistical difference

between the results of tests run on separate days for the zero ozone dosage (aeration only). One possible explanation for the statistical difference shown for Column 6 is implied in Table 15. The raw-water jar-test results corresponding to those of the 12 mg/l ozonated samples had settled turbidity values ranging from 20 to 25 NTU's. While these values were higher than the initial raw-water turbidity, they were also much higher than those of other settled raw-water jar-test samples in Column 6. Such instances of variability could very well cause the ANOVA results.

Table 17 shows the ANOVA results for the ozonated raw-water jar-test samples (Column 7). This analysis did not indicate a difference due to ozone dose. However, a difference due to the date within the dose (at 0 mg/l ozone) was observed. A possible explanation for the difference again can be obtained from Table 15. Reference to the aerated sample data shows that the June 19 jar test resulted in turbidity values which were apparently much higher than those measured for the June 23 and June 24 samples. Thus, a difference existed which could have been detected in the ANOVA procedure. Furthermore, the June 19 aerated jar-test turbidity values (Column 7) were higher than those recorded for the corresponding raw-water sample (Column 6). Inconsistency was obvious when the June 23 and June 24 results conversely indicated that the raw-water settled samples (Column 6), rather than the aerated settled jar-test samples (Column 7), had the higher residual turbidity.

Because of such variability and inconsistency, no further statistical evaluation was attempted. However, a few additional observations seem appropriate. The results of the jar tests are graphed in Figure 20. The average recorded turbidity values of the treated raw-water samples, excluding that at the initial 24 mg/l applied ozone dosage, were higher than those of corresponding samples initially treated with ozone. However, because of the illogical results previously mentioned (comparing Columns 6 and 7) for certain individual samples in Table 15, the results of selected tests were not plotted.

Other inconsistencies can be noted. A case in point is the variability exhibited in the raw-water jar-test samples (Column 6) at the 16 mg/l ozone dosage. Table 15 shows that turbidity values of 11.0, 9.0, and 4.5 NTU's were measured for samples that should have had the same turbidity. As a result, the average turbidity plotted in Figure 20 is much higher than that of corresponding samples (excluding that plotted for the 16 mg/l dosage).

Questionable results were again noted at the 24 mg/l dosage. While the initial run resulted in higher turbidity readings for the treated ozonated raw-water samples (Table 15, Column 7), Figure 20 indicates that the opposite was true for the optimum run, for which the treated raw-water sample had the higher average turbidity.

Because aeration alone may have resulted in turbidity reduction, it is impossible to determine from the available data whether simple aeration or ozonation favorably affects flocculation. A possible reason for the apparent variability and inherent inconsistency is that certain water samples could have been collected during periods of slug river

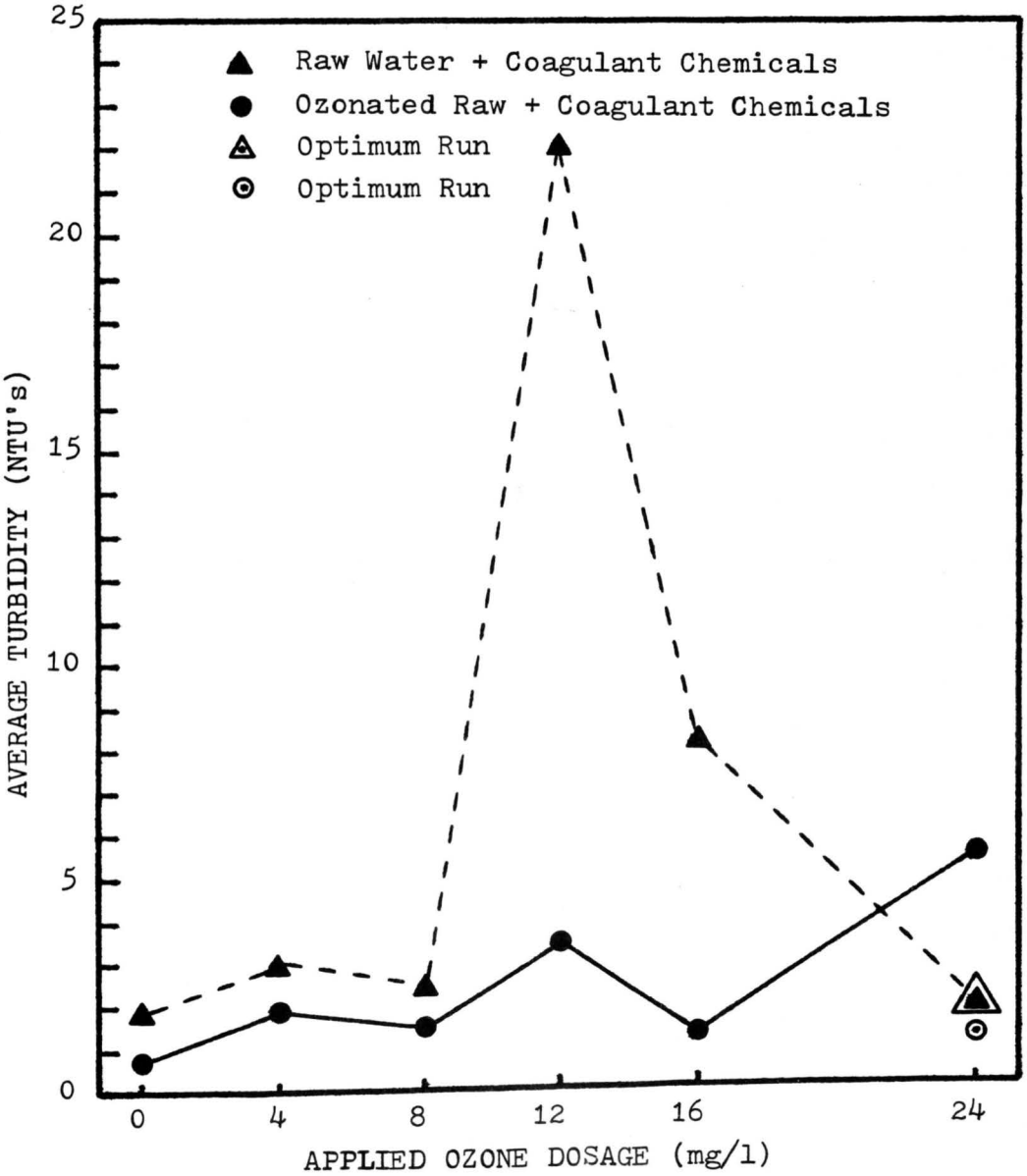


Figure 20. Settled Jar-Test Sample Turbidity Values

flows, which in turn would have led to errors in the experimental results.

Figure 21 is a bar graph of the optimum run results. An apparent reduction in sample turbidity is indicated when comparing the raw sample plus coagulant chemicals to the raw sample plus all chemicals. However, a comparison of Columns 5 and 6 in Table 15 indicates the opposite for the same tests carried out during the 16 mg/l ozone dosage run. During that run, the raw sample treated with all chemicals had an average turbidity of 25 NTU's while the raw sample treated with coagulant chemicals had an average turbidity of 8.2 NTU's. Thus, a statement regarding the effectiveness of all chemicals relative to coagulant chemicals for flocculation enhancement cannot be made. Similarly, a valid conclusion regarding the effectiveness of ozonated raw water treated with coagulant chemicals over raw water treated with all chemicals cannot be made based on the available data, as previously discussed.

Although turbidity removal was not proven to be enhanced by ozonation, some observations of favorable flocculation and settling characteristics were made. It was observed that the floc in the ozonated samples, especially at the higher ozone dosages, formed more quickly and settled more readily than did that of unozonated samples. In addition, the ozonated samples appeared to form larger floc particles than did the unozonated samples.

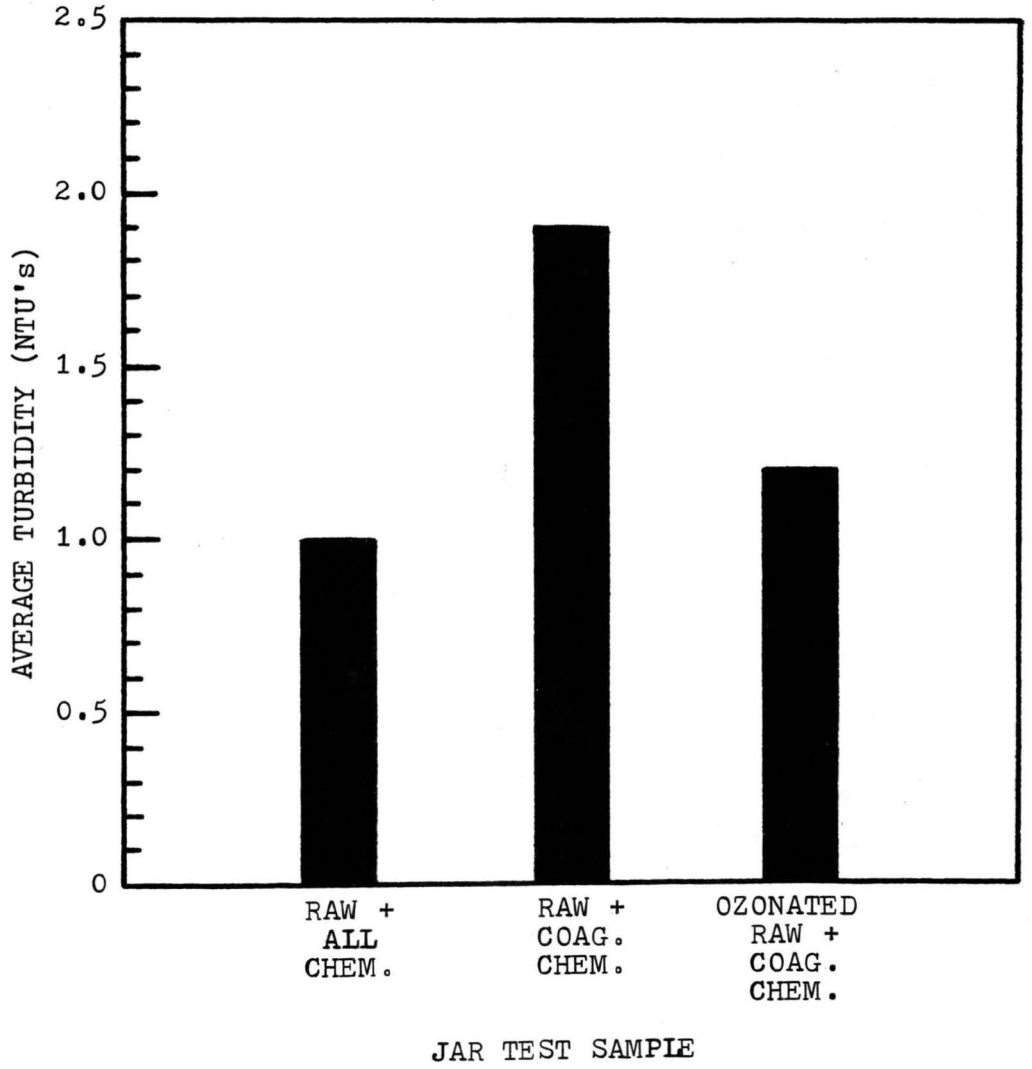


Figure 21. Settled Jar-Test Sample Turbidity Values for the Optimum Run (24 mg/l Ozone Dosage)

Estimation of Ozonation Costs

In estimating the cost of constructing and operating an ozonation system at Huron, cost curves and procedures developed by the United States Environmental Protection Agency (EPA) (11) were utilized. Because the cost curves were based on October, 1978, values, the individual figures were updated through use of Engineering-News Record (6) and Bureau of Labor Statistics (41) indices found in Appendix D, Table D1.

The total cost was divided into three segments: construction cost of the contact chamber; construction cost of the ozone generation system; and annual operation and maintenance cost. Each of these segments was in turn subdivided into more specific categories for cost estimation. Appendix D contains sample calculations and specific tabulations.

The cost estimates are based on a design flow of 2 MGD and a contact chamber detention time of 20 minutes. In addition, final calculations were made for an extremely conservative applied ozone dosage, 24 mg/l. At this flow and dosage, an ozone generation capacity of 400 lb/day and a contact chamber volume of 3,710 cubic feet were required.

The EPA curves used to determine the construction cost of the ozone contact chamber were based on several assumptions. For example, it was assumed that the chamber was a covered, reinforced concrete structure with a depth of 18 feet and a length-to-width ratio of 2:1. Partitions were utilized within the chamber to promote uniform ozone distribution. Dissolution equipment costs were also included in the cost curve. A

summary of the cost estimate for the contact chamber is presented in Appendix D, Table D2.

In calculating the ozone generation system construction cost, pure oxygen was assumed to be the feed-gas. The manufactured equipment costs listed in Appendix D, Table D3, included the gas preparation equipment, oxygen generation equipment, the ozone generator, dissolution equipment, off-gas recycling equipment, electrical and instrumentation costs, and all required safety and monitoring equipment. All ozone-generating equipment was considered to be housed, but the oxygen-generating equipment was located outside on a concrete slab.

For the oxygen-fed ozone generation system, a power demand of 7.5 kW-hr/lb of ozone generated was assumed. In addition, the operation cost curve provided for oxygen generation, ozone generation, and ozone dissolution. In determining the annual energy cost, a range of $0.03/kW-hr to $0.07/kW-hr was used. Although the exact energy cost at Huron is dependent upon factors such as time of usage and variation in energy demand, it is assumed that the actual cost would be within this range. Maintenance materials and necessary labor requirements were also considered in the annual operation and maintenance cost estimate. A summary of the estimated costs of operation and maintenance for the anticipated maximum and minimum power costs may be found in Appendix D, Table D4.

Based on the design flow of 2 MGD and ozone dosage of 24 mg/l for 20 minutes, the estimated costs of ozonation are presented in Table 18. All costs were adjusted to October, 1981. From this table, it can be seen that the construction cost was estimated to be $869,000 while the

Table 18. Estimated Construction, Operation and Maintenance Costs

Cost Components	Construction Costs ($)			Annual Operation and Maintenance Costs ($/yr)	
	Contact Chamber	Generation System	Total	@ 3¢/kW-hr	@ 7¢/kW-hr
Concrete	5,566	1,114	6,680		
Electrical Energy				33,390	77,910
Excavation and Sitework	1,788		1,788		
Housing		18,219	18,219		
Labor	12,379	111,817	124,196	8,800	8,800
Steel	9,170	1,170	10,340		
Manufactured Equipment		594,563	594,563		
Maintenance Materials				8,357	8,357
Miscellaneous and Contingency	4,335	109,032	113,367		
TOTAL COST	33,000	836,000	869,000	50,000	95,000

Note: Design water flow rate = 2 MGD
Selected applied ozone dosage = 24 mg/l
Contact chamber detention time = 20 minutes

Cost curves and procedures outlined in Estimating Water Treatment Costs (11) were utilized in developing cost data.
All costs were updated to October, 1981

annual operation and maintenance cost was estimated to range from $50,000 (6.8¢/1,000 gal) to $95,000 (13.0¢/1,000 gal) at electricity rates of $0.03/kW-hr and $0.07/kW-hr, respectively.

Because of the current fluctuations in interest rates, the total annual costs were calculated for rates from 5 to 20 per cent (10) and are presented in Table 19. It should be noted that these costs were developed using general parameters which were not site specific. Therefore, the resultant figures serve only as preliminary cost estimations.

During 1980 and 1981, the Huron plant treated an average flow of 2.0 MGD*. During this period, approximately $40,000 was spent each year for odor removal chemicals (activated carbon and potassium permanganate). Annual costs for disinfection chemicals (chlorine and ammonium sulfate) were in the range of $20,000. Furthermore, Huron currently spends slightly over $10,000 for alum per annum. Based on the studies presented herein, it would appear that ozonation could eliminate the need for activated carbon and potassium permanganate. As previously noted, ozone was reasonably effective in reducing odors at applied dosages as low as 4 mg/l. Ozone is also a strong disinfectant, much stronger than chlorine (31). Thus, the use of ozone would be expected to reduce chlorine requirements and eliminate the need for ammonium

*personal communication with Harold Root, Huron Water Treatment Plant Superintendent.

Table 19. Estimated Annual Ozonation Costs at Various Interest Rates

Interest Rate (%)	Capital Recovery Factor	Annual Repayment on Construction Cost ($/yr)	Total Annual Cost as of October, 1981			
			@ 3¢/kW-hr		@ 7¢/kW-hr	
			$/yr	¢/1,000 gal	$/yr	¢/1,000 gal
5	0.08024	69,700	119,700	16.4	164,700	22.6
6	0.08718	75,800	125,800	17.2	170,800	23.4
7	0.09439	82,000	132,000	18.1	177,000	24.2
8	0.10185	88,500	138,500	19.0	183,500	25.1
9	0.10955	95,200	145,200	19.9	190,200	26.1
10	0.11746	102,100	152,100	20.8	197,100	27.0
12	0.13388	116,300	166,300	22.8	211,300	28.9
14	0.15099	131,200	181,200	24.8	226,200	31.0
16	0.16867	146,600	196,600	26.9	241,600	33.1
20	0.20536	178,500	228,500	31.3	273,500	37.5

Note: Total Construction Cost = $869,000
Annual Operation and Maintenance Cost :
$50,000 @ 3¢/kW-hr = 6.8¢/1,000 gal
$95,000 @ 7¢/kW-hr = 13.0¢/1,000 gal

Capital Recovery Factor (CRF) values were taken from interest tables found in Principles of Engineering Economy (10).

sulfate. Ozone has also been shown to decrease alum requirements (23) (27). However, in the investigations presented herein, the effects of only one alum dosage, 22 mg/l (Appendix B, Table B1) were evaluated in conjunction with other plant chemicals. Reference to Appendix D, Table D4, indicates that the ozonation process at 24 mg/l requires an estimated 1,100,000 kW-hr/yr for a 2-MGD water flow and at a 20-minute contact time. This amount of electrical energy would cost from $33,000 to $77,000 per year at the rates of $0.03/kW-hr and $0.07/kW-hr, respectively.

It should be emphasized that the optimum applied ozone dosage of 24 mg/l used in the cost estimates is an extremely high dosage when compared to dosages reported in the literature for odor control (9)(23) (45). As mentioned previously, an ozone production rate of 400 lb/day is needed to obtain a dosage of 24 mg/l at a flow rate of 2 MGD. If this production rate was held constant at 400 lb/day, ozone dosages resulting from flows ranging from 1 to 8 MGD are presented in Table 20. It is apparent from the table that an ozone dosage of 24 mg/l at a 2-MGD flow (the average flow at the Huron plant) equates to an applied ozone dosage of 7 mg/l at 7 MGD, the plant design capacity. As previously noted in Table 8, Table 10, and Figure 14, applied ozone dosages of 4 and 8 mg/l not only caused a significant odor reduction for a poor quality water but also changed its characteristic odor from an unpleasant, fishy one to one characterized as being sweet and pleasant.

Table 20. Ozone Dosages for Various Water Flow Rates Based on a Total Ozone Output of 400 lb/day

Applied Ozone Dosage (mg/l)	Water Flow Rate (MGD)
48	1
24	2
16	3
12	4
10	5
8	6
7	7
6	8

Note: Contact Chamber Volume = 3,710 cubic feet

CONCLUSIONS

The following conclusions were made in regard to this research:

1. Ozone consistently changed the characteristic odor of the raw water from one described as "fishy" to one described as "pleasant" or "sweet".

2. Aeration did not change or reduce the odor of the raw water.

3. TON's of the raw water were reduced at all ozone dosages except 12 and 16 mg/l.

4. Ozone dosages of 4 or 8 mg/l are probably adequate for most odor applications at Huron.

5. Activated carbon and potassium permanganate were not effective at the dosages used in reducing or changing the raw-water odor.

6. The coagulation-flocculation-sedimentation processes reduced odor intensity but did not change the characteristic odor of the raw water.

7. Because of the variability and inconsistency of the jar-test data collected during the flocculation study, a valid conclusion regarding ozone's effectiveness in reducing turbidity could not be made.

8. Ozonated raw water, at the higher dosages, produced larger floc particles that formed more quickly and settled more readily than in corresponding samples of untreated water.

RECOMMENDATIONS

1. Based on comparative figures and ozone's multi-purpose applications, ozone should be given consideration as a treatment alternative at the Huron Water Treatment Plant.

2. Since algal blooms in surface waters are seasonal, an ozonation installation must be sized for normal demand plus consideration for the seasonal algae demand.

3. The construction cost of an ozonation system for Huron was estimated to be $869,000.

4. The annual operation and maintenance cost of the ozonation system was estimated to range from $50,000 to $95,000.

5. Based on energy requirements, the ozonation process costs alone were estimated to range from $33,000 to $77,000 annually.

FUTURE STUDIES

The following recommendations are made for future studies involving similar research objectives:

1. In addition to raw water, it is recommended that water from within the treatment process, such as sedimentation basin effluent, be subjected to ozonation. Because of prior turbidity removal, small ozone dosages may have a significant effect on parameters such as chlorine demand and odor reduction.

2. Several recommendations are suggested for the jar-test procedure:

   a) Settling times could be varied and comparisons made between ozonated and unozonated sample turbidity values.

   b) Chemical dosages could be varied to determine if lower chemical dosages result in equal or lower residual turbidity in the ozonated samples.

   c) To insure representative sampling, turbidity samples could be obtained through a port in the side of the jar rather than breaking the water surface to siphon a sample from within the jar-test sample.

3. It is recommended that zeta potential be considered as an alternative to the jar test turbidity in analyzing flocculation enhancement via ozonation.

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APPENDIX A

Selected Symbols and Abbreviations

Selected Symbols and Abbreviations

A.C. = activated carbon

ALL CHEM = all of the chemicals used at the Huron plant up through the solids contact basin

$\overset{o}{A}$ = angstroms

ANOVA = Analysis of Variance

@ = at

cm = centimeter

¢ = cents

COAG CHEM = coagulant chemicals used at the Huron plant up through the solids contact basin

cfs = cubic feet per second

m^3/s = cubic meters per second

DDT = dichlorodiphenyltrichloroethane

^oC = degrees Centigrade

^oF = degrees Fahrenheit

DC = direct current

$ = dollars

EPA = Environmental Protection Agency

ft = feet

gal = gallons

gpm = gallons per minute

Hz = Hertz

in = inch

kg = kilograms

kPa = kilopascals

kV = kilovolts

kW = kilowatt

kW-hr = kilowatt hours

lpm = liters per minute

m = meters

mg/l = milligrams per liter

ml = milliliters

mm = millimeters

MGD = million gallons per day

NTU = Nephelometric Turbidity Unit

N = normal

ppm = parts per million

% = per cent

** = 99 per cent confidence level

PAO = phenylarsine oxide

PVC = polyvinylchloride

KI = potassium iodide

$KMnO_4$ = potassium permanganate

lb = pounds

psig = pounds per square inch, gage

rpm = revolutions per minute

$Na_2S_2O_3$ = sodium thiosulfate

scfm = standard cubic feet per minute

slpm = standard liters per minute

TON = threshold odor number

APPENDIX B

Experimental Calculations

Experimental Calculations

A. Ozone Concentration

$$C = (\text{Wt } O_3)/V_1$$

where: C = ozone concentration in gas (mg/l)

Wt O_3 = weight of ozone trapped in potassium iodide solution (mg)

$$= \left(\frac{\text{N mole}}{\text{liter}}\right)(\text{ml titrant})\left(\frac{24 \text{ g } O_3}{\text{mole}}\right)\left(\frac{\text{liter}}{1000 \text{ ml}}\right)\left(\frac{1000 \text{ mg}}{\text{g}}\right)$$

$$= (N)(\text{ml titrant})(24)$$

where: N = normality of sodium thiosulfate titrant

V_1 = corrected volume of gas measured by the wet-test meter (liters)

$$= (V_2)(P_1/P_2)(T_2/T_1)$$

where: V_2 = actual volume of gas measured by the wet-test meter (liters)

P_1 = adjusted pressure = atmospheric pressure + wet-test meter manometer deflection - water vapor pressure (from Figure B1)

= ____ cm H_2O

P_2 = standard pressure = 1 atmosphere = 1033 cm H_2O

T_1 = room temperature (^oK)

T_2 = standard temperature = 298 ^oK

B. Gas Flow Rate

$$Q = (Q_1)(P_3/P_4)(T_3/T_1)^{\frac{1}{2}}(T_2/T_3)$$

where: Q = corrected gas flow rate (standard liters/minute)

Q_1 = actual gas flow rate (liters/minute)

P_3 = gage backpressure + barometric pressure (mm Hg)

P_4 = calibration gage pressure + standard pressure = 776 mm Hg + 760 mm Hg = 1536 mm Hg

T_3 = calibration temperature = 294 ^oK

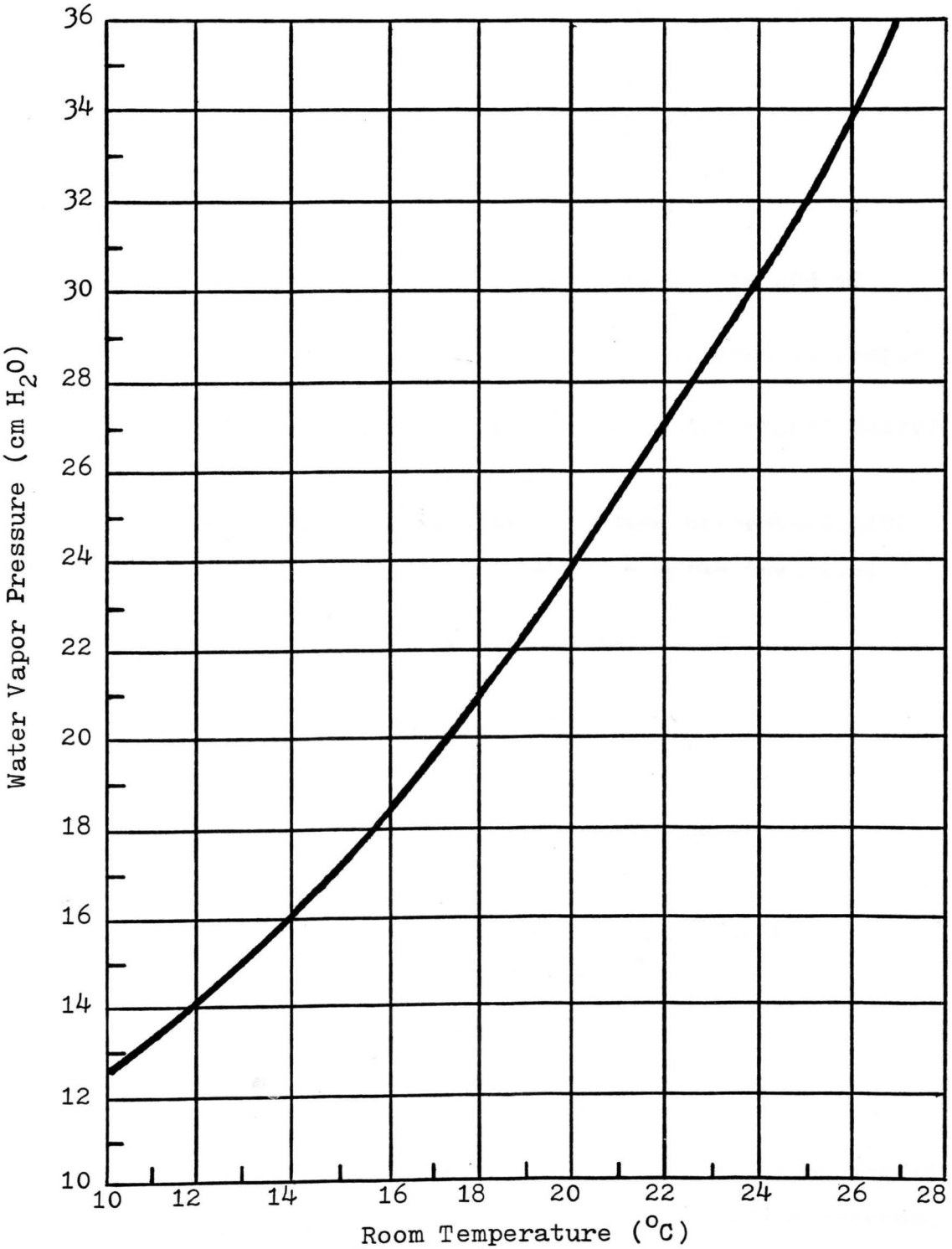

Figure B1. Water Vapor Pressure versus Temperature

C. Applied Ozone Dosage

$$D = (C)(Q/Q_w)$$

where: D = applied ozone dosage (mg O_3/liter H_2O)

Q_w = water flow rate (liters/minute)

D. Ozone Residual

$$O_3 = \left[(PAO) - (K)(I)\right](0.677)$$

where: O_3 = ozone residual by back titration in 200 ml sample (mg/l)

PAO = volume of phenylarsine oxide placed in sample container (ml)

K = titrant strength factor (to be determined daily)

$= (N_I)/(N_{PAO})$

where: N_I = normality of iodine titrant $\sim$ 0.0282

N_{PAO} = normality of phenylarsine oxide = 0.00564

I = volume of iodine titrant (ml)

E. Threshold Odor Number

$$TON = \left[(TON_1)(TON_2)(TON_3)\ldots(TON_n)\right]^{1/n}$$

where: TON = panel threshold odor number

TON_i = individual threshold odor numbers

$= B/A$

where: B = total test volume = 200 ml

A = sample volume (ml)

n = number of panelists

F. Chemical Dosages for Jar Tests

$$C_a = (C_b)(V_b)/(V_a)$$

where: C_a = chemical concentration of stock solution (mg/l)

C_b = average chemical concentration used in treatment plant and jar tests (mg/l)

V_a = volume of stock solution to be added to jar test sample (ml)

V_b = sample volume (1000 ml) + V_a

Table B1. Jar-Test Chemicals				
Chemical	C_a	C_b	V_a	V_b
$KMnO_4$	603	3	5	1,005
Activated Carbon	1,212	12	10	1,010
Alum	2,222	22	10	1,010
Nalco #8102	281.4	1.4	5	1,005
Lime	27,775	275	10	1,010
Nalco #2	1,515	15	10	1,010
Nalco #8184	300.3	0.3	1	1,001

C_a = chemical concentration of stock solution (mg/l)

C_b = average chemical concentration used in treatment plant and jar tests (mg/l)

V_a = volume of stock solution to be added to jar test sample (ml)

V_b = sample volume (1,000 ml) + V_a

APPENDIX C

Experimental Data

Table C1. Preliminary Results: Instantaneous Trihalomethane Data

Applied Ozone Dosage (mg/l)	Contact Column Detention Time (minutes)				
	5	10	15	20	30
4	91.3 (17.9)		81.8 (26.4)	73.2	69.1
8	56.5 (45.8)	89.9 (19.2)	65.9 (40.7)	34.9 (48.1)	128.0
12		44.3 (57.5)	20.0 (32.9)	<26.5 (60.6)	30.6 (54.5)
16		52.8 (49.4)	23.8 (64.6)	25.3 (62.4)	74.3 (33.1)
24			29.3 (71.9)	33.3 (68.1)	24.9 (62.9)
30					31.9 (31.9)

Note: ____ Indicates Instantaneous Trihalomethane Values (micrograms per liter)

( ) Indicates Trihalomethane Reduction (per cent from appropriate raw data)

ANALYSES WERE CONDUCTED BY THE SOUTH DAKOTA STATE UNIVERSITY BIOCHEMISTRY LAB, GAS CHROMATOGRAPHY PROCEDURE

Table C2. Ozone Contacting and Generator Calibration Data

Applied Ozone Dosage (mg/l)	Testing Date (1981)	Ozone Residual (mg/l)	Absorbed Ozone Dosage (mg/l)	Ozone Demand (mg/l)	Contacting Efficiency (per cent)	Maximum Generator Voltage (per cent of)	Input Voltage (volts)	Number of Dielectric Tubes in Generator
4	6/22 *	0	3.42	3.42	92	59	141	1
	7/8 **	0	3.61	3.61	90	55	130	3
8	6/25 *	0	7.22	7.22	85	59	140	3
	7/8 **	0	7.30	7.30	85	60	141	3
12	6/19 *	0.30	10.17	9.87	90	70	165	1
	7/13 **	0.09	11.91	11.82	91	62	147	3
16	6/18 *	0.82	12.25	11.43	83	95	229	1
	7/13 **	0.38	13.08	12.70	80	67	155	3
24	6/24 *	0.69	20.30	19.61	84	95	229	3
	7/6 **	0.66	19.86	19.20	91	95	229	3
24 Optimum	7/16	0.71	20.83	20.12	91	95	225	3

Note: * Indicates Flocculation Enhancement Run
** Indicates Odor Control Run

Contact Column Detention Time = 20 Minutes

Table C3. Selected Raw Water Quality Data

Date (1981)	Applied Ozone Dosage (mg/l)	Raw Water Quality Parameter Values						
		pH (Units)	Temperature (^{o}C)	Turbidity (NTU's)	Conductivity (mhos)	Total Organic Carbon (mg/l)	Hardness (mg/l as $CaCO_3$)	Alkalinity (mg/l as $CaCO_3$)
6/18	16	8.4 (8.2)	20 (20)	21 (25)	1400 (1400)	16.5, 15.4	488	376
6/19	0	8.4 (8.4)	20 (20)	19 (19)	1400 (1400)	15.5, 15.8	480	400
	12	8.4 (8.4)	20 (20)	19 (17)	1400 (1400)			
6/22	4	8.4 (8.4)	22 (22)	24 (22)	1400 (1400)			
	4	8.4 (8.4)	22 (22)	24 (22)	1400 (1400)			
6/23	0	8.4 (8.4)	23 (23)	35 (43)	1400 (1400)			
6/24	24	8.4 (8.1)	23 (23)	20 (18)	1400 (1400)	17.0, 17.0	480	376
6/25	8	8.3 (8.3)	23 (23)	29 (29, 25, 27)	1430 (1430)	16.5, 17.0	468	384
7/1	0	8.5 (8.5)	26 (26)	21 (76)	1400 (1400)			
7/2		8.5					480	416
7/6	24	8.5	26	21	1400			
7/7		8.4					460	412
7/8	4	8.5	24	17	1400			
	8	8.5	24	17	1400			
7/11		8.5					480	456
7/13	12	8.6	29	18	1500			
	16	8.6	29	18	1500			
7/16	24	8.6 (8.3)	27 (27)	23, 28, 29 (53)	1450 (1800)	20.7, 20.0	480	468

Note: ( ) Indicates Corresponding Ozonated Raw Water Values

Table C4. Threshold Odor Test Results

Water Sample	Collection Date (1981)	Individual Threshold Odor Numbers						Panel TON		General Characteristic Odor
		Dornbush	Graber	Hadi	Nusz	Rollag	Van Hout	Geometric Mean	Raw Mean	
Raw	7/1	8.0	11.8	8.0	8.0	8.0	16.7	9.6	10.1	Fishy
Ozonated Raw (0 mg/l)	7/1	8.0	11.8	16.7	11.8	8.0	16.7	11.6	12.1	Fishy
Raw	7/8	24.1	16.7	24.1	24.1	24.1	24.1	22.7	22.9	Fishy
Ozonated Raw (4 mg/l)	7/8	11.8	16.7	24.1	11.8	16.7	16.7	15.8	16.3	Sweeter
Raw	7/8	24.1	24.1	24.1	24.1	24.1	24.1	24.1	24.1	Fishy
Ozonated Raw (8 mg/l)	7/8	16.7	16.7	24.1	16.7	16.7	24.1	18.8	19.2	Sweet
Raw	7/13	16.7	16.7	11.8	24.1	11.8	16.7	15.8	16.3	Fishy
Ozonated Raw (12 mg/l)	7/13	35.1	24.1	24.1	24.1	16.7	24.1	24.1	24.7	Sweet
Raw	7/13	24.1	16.7	11.8	24.1	8.0	24.1	16.7	18.1	Musty
Ozonated Raw (16 mg/l)	7/13	11.8	11.8	11.8	11.8	16.7	16.7	13.2	13.4	Sweet
Raw	7/6	11.8	24.1	24.1	24.1	24.1	16.7	20.1	20.8	Fishy
Ozonated Raw (24 mg/l)	7/6	5.7	8.0	2.9	2.9	11.8	5.7	5.4	6.2	Sweet
Presed. Basin Eff.	7/6	16.7	35.1	16.7	35.1	16.7	16.7	21.4	22.8	Musty
Solids Contact Eff.	7/6	11.8	11.8	11.8	11.8	11.8	11.8	11.8	11.8	Fishy
Raw	6/29	5.7	8.0	8.0	5.7	11.8	8.0	7.6	7.9	Fishy
Raw + Activated Carbon	6/29	5.7	24.1	5.7	11.8	11.8	5.7	9.2	10.8	Fishy
Raw + $KMnO_4$	6/29	8.0	11.8	11.8	8.0	8.0	16.7	10.3	10.7	Fishy
Raw + Act. Car. + $KMnO_4$	6/29	8.0	11.8	8.0	11.8	11.8	11.8	10.3	10.5	Fishy
Raw	7/16		24.1	35.1	71.4	35.1	50.0	40.3	43.1	Fishy
Raw + Coag. Chem.	7/16		35.1	11.8	35.1	24.1	35.1	26.2	28.2	Fishy
Raw + All Chem.	7/16		16.7	16.7	24.1	16.7	16.7	18.0	18.2	Fishy
Ozonated Raw (24 mg/l)	7/16		11.8	24.1	11.8	16.7	16.7	15.6	16.2	Sweet
Ozonated + Coag. Chem.	7/16		16.7	11.8	16.7	11.8	16.7	14.5	14.7	Sweet

Table C5. Water Quality Data for Optimum Run Testing

Sample	pH (units)	Temperature (°C)	Turbidity (NTU's)	Conductivity (mhos)	Total Organic Carbon (mg/l)
Raw Water	8.6	27	23, 28, 29	1450	20.7, 20.0
Ozonated Raw	8.3	27	53	1800	19.9, 20.0
Presed. Basin Eff.	8.8	27	14	1450	21.1, 21.6
Solids Contact Eff.	10.4	27	2.7	1220	13.4, 12.2
Raw + All Chem. (Jar Test)	10.4	21	0.85, 1.0, 1.1, 1.2, 1.0	1210	14.1, 14.5
Raw + Coag. Chem. (Jar Test)	10.3	21	1.8, 1.8, 1.8, 2.0, 2.0, 2.0	1220	14.8, 15.5
Ozonated + Coag. Chem.	10.1	21	0.95, 1.4, 1.4, 1.3, 0.94, 0.96	1225	14.3, 14.9

Note: "Optimum Run" testing occurred on July 16, 1981, at an applied ozone dosage of 24 mg/l.

Copper sulfate bags were dragged in the river during the morning hours to treat a major algae bloom.

Ozonated jar test samples developed very large floc particles, as observed previously, especially at ozone dosages of 16 and 24 mg/l.

APPENDIX D

Estimation of Ozonation Costs

Estimation of Ozonation Costs

Assumptions: Design water flow rate = 2 MGD

Selected applied ozone dosage = 24 mg/l

Contact chamber detention time = 20 minutes

Calculation of Total Annual Ozonation Cost

$$TC_a = C_a + OM_a$$

where: TC_a = total annual cost of ozonation ($)

C_a = annual construction cost repayment ($)

$= (CRF)(C_p)$

where: CRF = capital recovery factor

$$= \frac{i}{(1 + i)^n - 1} + i$$

where: i = annual interest rate (decimal)

n = number of repayment years

= 20

C_p = total construction cost ($)

OM_a = annual operation and maintenance cost ($)

$= (EED)(ER) + MM + L$

where: EED = electrical energy demand (kW-hr/yr)

ER = electricity rate ($/kW-hr)

MM = annual maintenance material cost ($)

L = annual labor cost ($)

Note: Cost curves and procedures outlined in Estimating Water Treatment Costs (11) were utilized in developing cost data. All costs were updated to October, 1981.

CRF values were taken from interest tables found in Principles of Engineering Economy (10).

Table D1. Cost Updating and Appropriate Indices

Cost Component	Cost Index	Index Value		Correction Factor
		October, 1978	October, 1981	
Excavation and Sitework	ENR Wage Index for Skilled Labor	247.0	319.0	1.29
Manufactured Equipment	BLS General Purpose Machinery and Equipment	221.3	294.4	1.33
Concrete	BLS Concrete Ingredients	221.1	298.3	1.35
Steel	BLS Steel Mill Products	262.1	348.7	1.33
Labor	ENR Wage Index for Skilled Labor	247.0	319.0	1.29
Housing	ENR Building Cost Index	254.76	319.12	1.25
Maintenance Materials	BLS Producer Price Index for Finished Goods	199.7	274.0	1.37

Note: ENR refers to Engineering News Record data (6)

BLS refers to Bureau of Labor Statistics data (41)

Table D2. Construction Cost of Ozone Contact Chamber as of October, 1981

Cost Category	Cost of Construction ($)	
	October, 1978	October, 1981
Excavation and Sitework	1,386	1,788
Concrete	4,123	5,566
Steel	6,895	9,170
Labor	9,596	12,379
Subtotal Cost	22,000	28,903
Miscellaneous and Contingency (15% of Subtotal)	3,300	4,335
Total Cost	25,300	33,238

Note: Design water flow rate = 2 MGD

Contact chamber detention time = 20 minutes

Contact chamber volume = 3,710 cubic feet

As stated in Water Treatment Plant Costs (11), the contact chamber depth is assumed to be 18 feet.

Table D3. Construction Cost of Ozone Generation System as of October, 1981

Cost Category	Ozone Generation Capacity			
	8 mg/l (133 lb./day)	12 mg/l (200 lb./day)	16 mg/l (267 lb./day)	24 mg/l (400 lb./day)
Manufactured Equipment ($)	281,066 (211,328)	378,358 (284,480)	475,651 (357,632)	594,563 (447,040)
Concrete ($)	527 (390)	709 (525)	891 (660)	1,114 (825)
Steel ($)	553 (416)	745 (560)	936 (704)	1,170 (880)
Labor ($)	52,859 (40,976)	71,156 (55,160)	89,454 (69,344)	111,817 (86,680)
Housing ($)	8,613 (6,890)	11,594 (9,275)	14,575 (11,660)	18,219 (14,575)
Subtotal Cost ($)	343,618 (260,000)	462,562 (350,000)	581,507 (440,000)	726,883 (550,000)
Miscellaneous and Contingency (15% of Subtotal) ($)	51,543 (39,000)	69,384 (52,500)	87,226 (66,000)	109,032 (82,500)
Total Cost ($)	395,161 (299,000)	531,946 (402,500)	668,733 (506,000)	835,915 (632,500)

Note: ( ) Indicates cost as of October, 1978

Table D4. Operation and Maintenance Cost Range as of October, 1981

Ozone Generation Rate		Electrical Energy Demand (kW-hr/yr)			Maintenance Material Cost ($/yr)		Labor Cost	Total Cost ($/yr)	
mg/l	lb./day	Building	Process	Total	October, 1978	October, 1981	$/yr	3¢/kW-hr	7¢/kW-hr
8	133	7,900	440,000	447,900	3,200	4,384	6,000	23,821	41,737
12	200	9,000	630,000	639,000	4,100	5,617	6,900	31,687	57,247
16	267	10,100	890,000	900,100	5,050	6,919	7,600	41,522	77,526
24	400	13,000	1,100,000	1,113,000	6,100	8,357	8,800	50,547	95,067

Note: Labor Rate = $10/hr

Total Operation and Maintenance Cost = (Electrical Energy Demand)(Electricity Rate) + Maintenance Material Cost + Labor Cost

Ozone Generation Rate (lb./day) = (mg/l)(2 MGD)(8.3453)

Total Operation and Maintenance Costs were calculated using given maximum and minimum electricity rates. The actual cost would be dependent upon factors such as time of usage and would occur within the above ranges.

APPENDIX E

Water Treatment at Huron

Water Treatment at Huron

History

The history of water treatment at Huron, South Dakota, has been summarized in part by Harms and Looyenga (15).

The first public water supply for Huron was the James River, a slow meandering stream that ranges in depth, width, flow, and overall water quality. In 1883, water was pumped directly from the James into the distribution system with no treatment. In 1886, the river water was replaced by water produced from four artesian wells. However, the artesian supply soon became inadequate to meet growing demand. As a result, the city switched back to the James River water in 1914, when a 1.5 MGD treatment plant was constructed to clarify and purify the water. The capacity was expanded to 3 MGD in 1928.

The 1930's drought caused the river supply to fall short of the demand. As a result, wells were again drilled and put into use in 1934. These wells produced a highly mineralized water and were sparingly used in conjunction with the river supply until 1951, when the wells alone were used for a short period of time.

A new 4 MGD water treatment plant was constructed in 1948 and 1949 for purification, clarification, and softening. But in 1959 and 1960, there was a shortage of James River water, forcing Huron to once again turn to the wells in order to meet the demand.

In 1964, the Bureau of Reclamation constructed the James Diversion Dam about fifteen miles north of Huron. Because the dam provided additional storage for Huron's water supply, the well fields were

abandoned. However, the drought conditions in 1981 caused Huron to again develop the wells as a supplementary source of drinking water.

The plant was extensively revised in 1977, resulting in a capacity increase to 7.4 MGD, the present capacity.

The Treatment Process

A schematic layout of Huron's water treatment plant is shown as Figure E1. Initially, raw water is pumped from the James River at an intake located about 100 feet upstream of the Third Street Diversion Dam. Upon entering the plant, potassium permanganate, activated carbon, alum, and a polyelectrolyte (Nalco #8102) are immediately added to the water and dispersed by mixing. Following presedimentation, lime, sodium aluminate (Nalco #2), soda ash (optional), and polyelectrolyte (Nalco #8184) additions are made at the center of the upflow basins, where solids are settled further. Following solids contact and settling, the water is subjected to pH adjustment with carbon dioxide in the recarbonation basin, after which it enters the chlorine contact chamber where chlorine and ammonium sulfate are added at the influent and effluent ends, respectively. Further chemical additions include fluoride and a polyphosphate (Nalco #918). After passing through anthrafilt gravity filters, the water is postchlorinated and temporarily stored in a clear-well before entering storage and the distribution system.

Chemical dosages are normally varied according to the raw water quality.

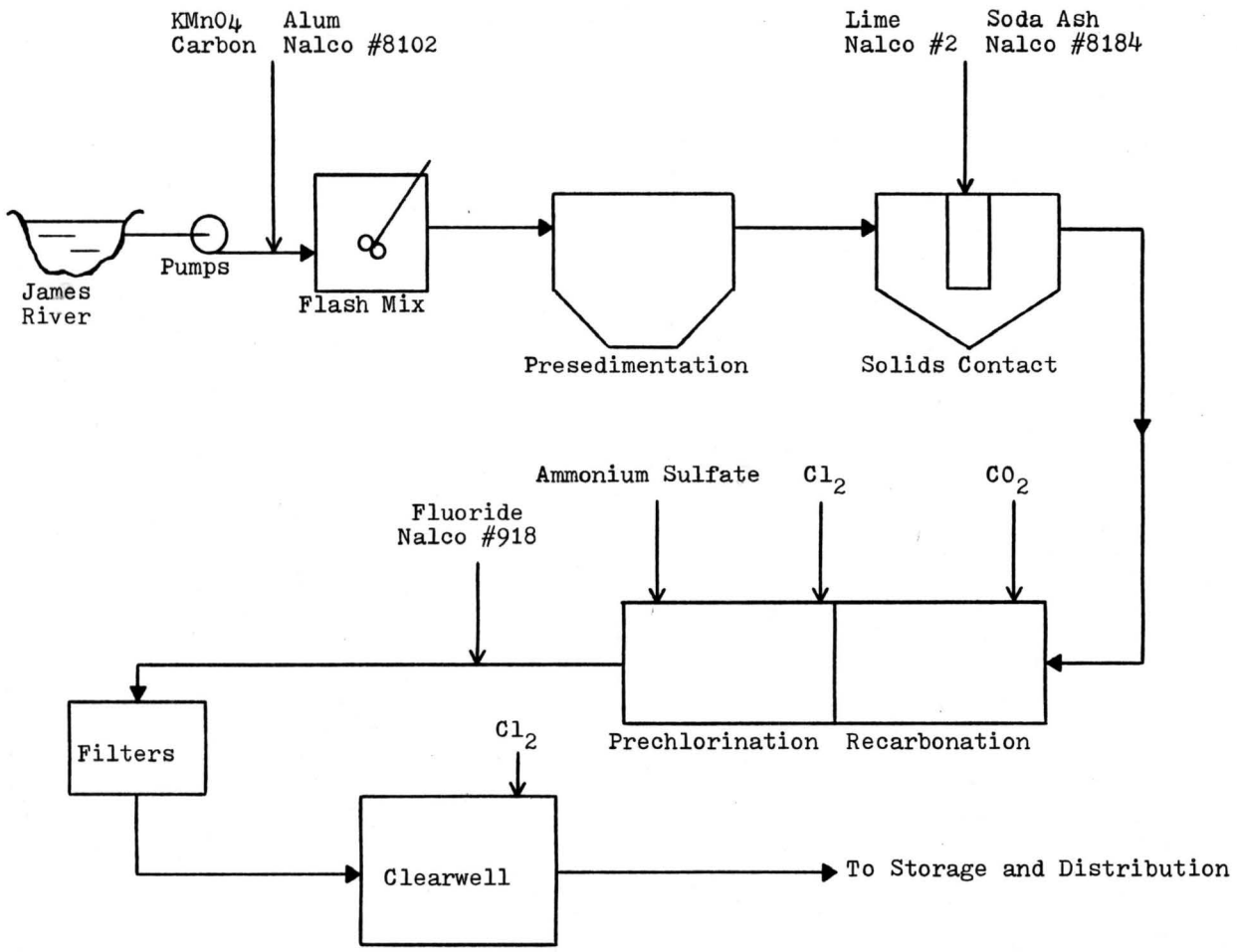

Figure E1. Flow Diagram of the Huron Water Treatment Plant